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TITLE OF THESIS..A..STUDY....OF..THE....PRODUCTION
..AND..CONTROL..OF..HYDROGEN..
...SULFIDE..FROM..ANAEROBIC..SWINE MANURE

UNIVERSITY.....University..of..Alberta.......................

DEGREE FOR WHICH THESIS WAS PRESENTED..M.Sc.(Ag...Eng.)

YEAR THIS DEGREE GRANTED....1974.....................

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THE UNIVERSITY OF ALBERTA

A STUDY OF THE PRODUCTION AND CONTROL OF HYDROGEN SULFIDE FROM ANAEROBIC SWINE MANURE

by

Ⓒ ERNEST MURRAY BARBER

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

DEPARTMENT OF AGRICULTURAL ENGINEERING

EDMONTON, ALBERTA

SPRING, 1974

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled "A Study of the Production and Control of Hydrogen Sulfide from Anaerobic Swine Manure" submitted by Ernest Murray Barber in partial fulfilment of the requirements for the degree of Master of Science.

J.B. McQuitty

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Date 15th February, 1974

ABSTRACT

Sulfur-containing gases produced during the anaerobic fermentation of livestock manure have been shown to be major components of the characteristic manure odor. Hydrogen sulfide also has been implicated as a principal offender in several human and animal casualties involving manure gases, and has been known to cause structural damage to metal and concrete components of livestock facilities.

An extensive review of the literature was conducted, therefore, to investigate factors affecting the production of sulfides in, and the desorption of hydrogen sulfude from, anaerobically fermenting manure. On the basis of this literature review, a series of exploratory trials were initiated to study lime, chemical oxidants, and various forms of iron as means of controlling the evolution of sulfur-containing gases from anaerobic swine manure. Furthermore, since sulfur-containing gases are produced from sulfur compounds in manure, a series of investigations were conducted to elucidate the sulfur status of fresh and fermented swine manure.

From an analysis of the data, the following results and conclusions were obtained:

1. Sulfur was excreted largely as organically-bound sulfur in the feces and as sulfate-sulfur in the urine of feeder pigs.
2. The sulfur status of the fresh excreta from feeder pigs, and the relative retention of sulfur and nitrogen by the pigs,were dependent upon the nature of the diet. The sulfur and nitrogen status of swine manure was largely dependent upon the class of swine from which the manure originated and

manure management practices.

3. Iron, added to manure either as ferrous salts or as finely powdered metallic iron, effectively reduced the evolution of hydrogen sulfide from the treated manure without adversely affecting the bacteria involved in the anaerobic digestion process.
4. Liming manure to maintain a pH greater than 10 was relatively effective in controlling the evolution of sulfides from anaerobic swine manure. Applications of lime apparently killed sulfate-reducing bacteria and reduced the rate of desorption of dissolved hydrogen sulfide from the manure solution.
5. Nitrate added to anaerobic swine manure effectively delayed the production of sulfides from the manure for several days.
6. At high rates of application, persulfate and permanganate prevented the evolution of sulfides from anaerobic manure by oxidizing dissolved sulfides to non-volatile sulfur compounds.
7. The relative effectiveness of each of the various chemicals for controlling the evolution of hydrogen sulfide from anaerobic swine manure was demonstrated in batch incubation trials. Before any of the chemicals can be recommended for application under field conditions, however, further testing in pilot-scale continuous-flow trials is necessary.

ACKNOWLEDGEMENT

Acknowledgement is made to all those persons involved in the preparation of this thesis.

The author is especially grateful to Professor J.B. McQuitty and Dr. F.D. Cook who freely gave their advice and criticism throughout this project. These two individuals provided the initial stimulus for, and guided the direction of, the investigations reported herein.

Aknowledgement is made to the technical staff of the Department of Soil Science, Animal Science, and Agricultural Engineering for the assistance they provided, particularly with sample analyses and construction of the necessary equipment. Sincere thanks are also extended to Miss Elsieanne Symons for the excellent job she made of typing the final draft of this manuscript.

The author is grateful to Messer's Ron and Reg Nelson, Elmer Goeglein and Sten Berg for allowing samples of manure to be collected from their hog production facilities. The cooperation and interest shown by these farmers is sincerely appreciated. Thanks are due, as well, to Dr. J.P. Bowland and his staff for supplying the fresh excreta samples used in this investigation.

The author also wishes to thank his wife, Phyllis, for her concern, understanding, and perserverance throughout the duration of his program.

Finally, acknowledgement is due to the Alberta Hog Producers Marketing Board and to the Alberta Environmental Research Trust for their financial support of this project.

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1. INTRODUCTION

Liquid manure systems have been used in Europe for many years and recently have become increasingly popular in North America. Handling manure as a fluid compared to handling it as a solid offers the advantages of lower labor requirements, more complete preservation of the fertilizer value of the manure, and greater adaptability to total confinement systems of livestock production. In Alberta, there appears to be a trend toward even greater acceptance of liquid manure systems, especially by hog producers.

Two quite different liquid manure systems used by Canadian farmers are those that incorporate a large storage pit beneath slatted floors and those that make use of flushing gutters with subsequent longer term storage of manure outside the livestock building. The latter system generally produces few problems with regard to animal health but odor problems from the outside storage facilities are quite common. The former system can result in high odor levels within the building and has been known to create conditions which are potentially dangerous to both animal and human occupants of the facility. The associated problems of odor and toxic gases currently are regarded as serious deterrents to more universal acceptance of liquid manure systems.

Toxic and malodorous gases associated with liquid manure are the result of the combined activities of several groups of bacteria which use manure constituents as substrates in their energy metabolism or as nutrients for cellular growth and reproduction. When manure is stored or treated under completely aerobic conditions, the organic portion of the manure, represented as $C_aH_bO_cN_dP_eS_f$, is oxidized by heterotrophic organisms to inorganic compounds as indicated by the following reaction:

$$C_aH_bO_cN_dP_eS_f + (a + 0.25b + 1.25d + 1.25e + 1.5f - 0.5c)O_2 \rightarrow aCO_2 + (0.5b - 0.5d - 1.5e - f)H_2O + dNO_3^- + ePO_4^{\equiv} + fSO_4^{=} + (d + 3e + 2f)H^+$$

The subscripts a,b,c,d,e and f represent the relative proportions of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), and sulfur (S), respectively, in the manure organics. In theory, the major gaseous emissions from manure that is maintained in the presence of excess dissolved oxygen are carbon dioxide (CO_2) and water vapour (H_2O). In practice, the oxidation of organic-nitrogen to nitrate-nitrogen (NO_3^-) is not always complete, the other inorganic nitrogeneous compounds produced being nitrite (NO_2^-) and ammonium (NH_4^+). In an aqueous media, ammonium is partially converted to ammonia (NH_3) which is volatile and may be released as a gas.

The bacterial degradation of organic matter in the absence of dissolved oxygen (anaerobic conditions) is slightly more complex than the aerobic process. For simplicity, the organic portion of manure may be considered to be composed of proteins, carbohydrates and fats. In the absence of dissolved oxygen, anaerobic bacteria decompose these organic constituents in a manner illustrated in Figure 1. As shown, the proteinaceous material is degraded to ammonia, hydrogen sulfide (H_2S) and short-chain organic acids. The degradation of carbohydrates proceeds initially with the production of organic acids which, together with the acids formed from proteins, are converted further to alcohols or degraded to water, carbon dioxide and short-chain hydrocarbons, including methane (CH_4). Fats are decomposed to fatty acids and

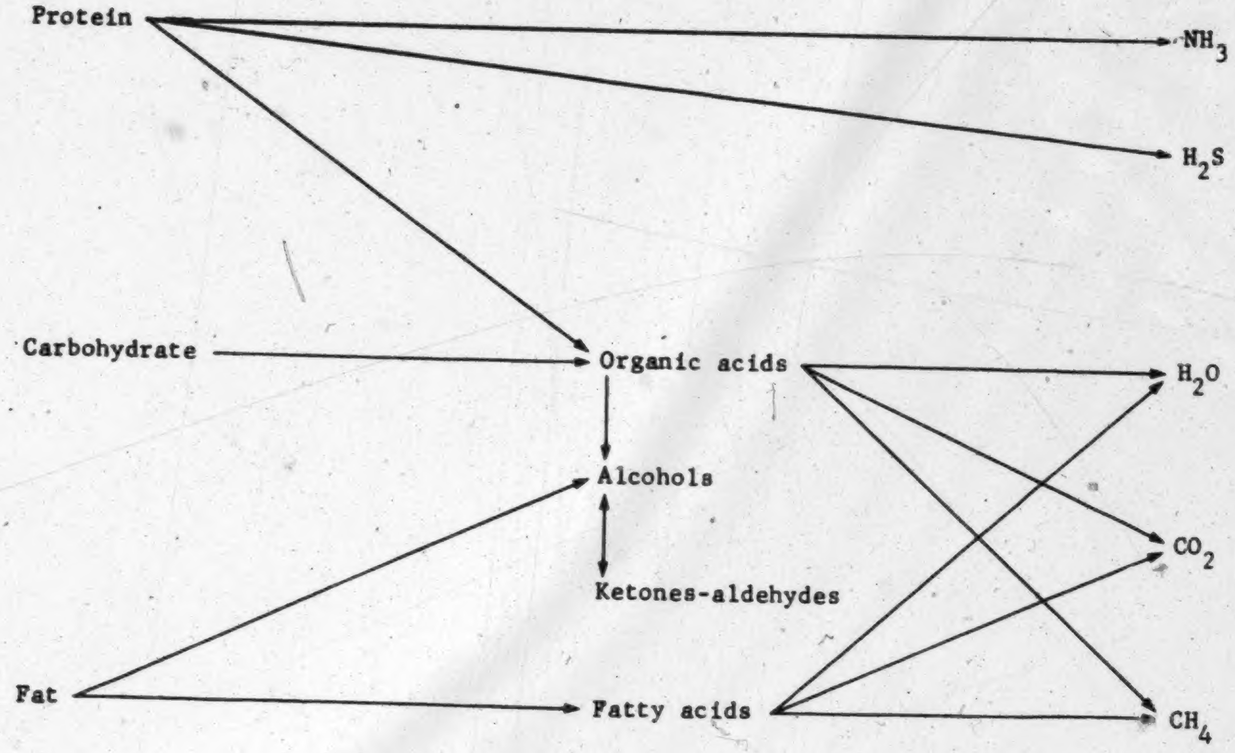

Protein
NH_3
H_2S
Carbohydrate
Organic acids
H_2O
Alcohols
CO_2
Ketones-aldehydes
Fat
Fatty acids
CH_4

Figure 1. Anaerobic degradation of manure organics.

alcohols, with the ultimate degradation of fatty acids to water, carbon dioxide and methane. Alcohols produced either directly from fats or indirectly from proteins and carbohydrates are subject to oxidation reactions resulting in the formation of aldehydes and ketones. Furthermore, ammonia can combine chemically, by displacement reactions, with alcohols (R - OH) and organic acids ($R' - C\genfrac{}{}{0pt}{}{=O}{-OH}$) to produce amines ($NH_2$ - R) and amides ($R' - C\genfrac{}{}{0pt}{}{=O}{-NH_2}$), respectively. Similarly, hydrogen sulfide can react with alcohols and organic acids to produce mercaptans (R - SH) and thioacids ($R' - C\genfrac{}{}{0pt}{}{=O}{-SH}$), respectively. Reactions between sulfides (formed in aqueous solutions containing dissolved hydrogen sulfide and the short-chain hydrocarbons also are possible, yielding disulfides (e.g., dimethyl sulfide). One further reaction of importance is that occurring between hydrogen sulfide and carbon dioxide to yield carbonyl sulfide. In summary, the major gaseous emissions resulting from the anaerobic degradation of manure organics are ammonia, carbon dioxide, water vapour, hydrogen sulfide, methane and other short-chain hydrocarbons, fatty acids, aldehydes and ketones, alcohols, amines, amides, mercaptans, disulfides, and carbonyl sulfide.

In addition to the aerobic and anaerobic degradation of the organic fractions of manure by heterotrophic bacteria, gases also may be produced from inorganic manure constituents. The organisms responsible utilize oxidized inorganic compounds as electron acceptors in their energy metabolism (e.g., sulfate reduction to hydrogen sulfide and nitrate reduction to ammonia and nitrogen gas). They may use either organic or inorganic compounds as nutrient sources and as electron sources in their energy metabolism and, on this basis, are classified as heterotrophs or autotrophs, respectively. The major gases produced by these bacteria are carbon dioxide, ammonia and hydrogen sulfide.

Of the gases produced by bacterial action on the organic and inorganic constituents of manure, those containing sulfur (hydrogen sulfide, carbonyl sulfide, mercaptans and disulfides) have been implicated as major components of the characteristic manure odor. Hydrogen sulfide also has been implicated as a principal offender in several human and animal casualties involving manure gases, and has been known to cause structural damage to metal and concrete components of livestock facilities. The major objectives of this study, therefore, were (a) by means of an extensive review of the literature, to investigate factors affecting the production of sulfides in, and the desorption of hydrogen sulfide from, anaerobically fermenting manure; and (b) on the basis of the findings of the literature review, to set up a series of exploratory trials to study alternate means of controlling the evolution of sulfide-containing gases from anaerobic manure.

2. LITERATURE REVIEW

2.1 Toxicity of Hydrogen Sulfide.

The major concern involving hydrogen sulfide in livestock buildings is associated with the deleterious effects the gas has on animal and operator health. Incidents involving deaths of farm animals by manure gas poisoning have been reported from Canada (88,103)[a], United States (84), Sweden (63), Ireland (80) and the Netherlands (55). Tragedies involving humans also have occurred. In 1968, two farm workers at Red Deer, Alberta were overcome when they entered a manure tank that was being pumped out (41). A similar case was reported in Ireland (78) in which a farmer and an agricultural contractor were killed upon entering a tank in which the slurry had been agitated. In all cases, the manure was being agitated at the time the deaths occurred, and in each case, the ventilation was assessed as being inadequate.

Concentrations of hydrogen sulfide in animal dwellings are normally very low or undetectable. Significant quantities of hydrogen sulfide in gutters or pits where manure was static have been recorded only when the manure originated from pigs (118). However, levels of hydrogen sulfide as high as 1000 ppm have been reported in the head-space areas above manure which was being agitated or pumped out (28,55,79).

The physiological responses of humans to various concentrations of hydrogen sulfide are presented in Table 1.

---

[a] Numbers in parenthesis refer to references listed in Section 8 - Literature Cited.

TABLE 1: PHYSIOLOGICAL RESPONSES OF HUMANS TO HYDROGEN SULFIDE.

Response	Concentration of Hydrogen Sulfide (ppm)
Slight symptoms after several hours.	100 - 150[a] 20 - 100[b]
Maximum for 1 hour without harm.	200 - 300[a]
Dangerous within 30 minutes.	500 - 700[a] 800 - 1000[b]
Rapidly fatal.	1000 - 3000[a] > 1000[b]

a - Henderson and Haggard (61).
b - McAllister and McQuitty (79).

MAC[a] values have been given as 20 ppm in some references (52,79,123) and as 10 ppm in others (28,90,93). McAllister and McQuitty (79) suggested that the reactions of farm animals to hydrogen sulfide will differ little from the physiological reactions by humans. However, since MAC values are based on exposure for an 8 - 10 hour period, lower values may need to be applied to livestock that are subjected to continuous exposure. Furthermore, the response of animals to hydrogen sulfide will depend on species and age (123). For example, younger or smaller animals will exhibit greater sensitivity to noxious gases than older or larger animals.

---

[a] MAC (maximum allowable concentration) is used to denote "such concentrations of various harmful chemical substances in the form of gases, vapours and dusts in industrial atmospheres, which, by their constant effect on workers during normal daily work over an indefinite period of time, can produce no pathological changes or disease detectable by current methods of examination" (73).

Humans exposed to high concentrations of hydrogen sulfide show symptoms of somnolence, amnesia, unconsciousness, delerium and hallucinations, along with difficulty in swallowing and low blood pressure, and will experience double vision and epileptiform convulsions (52). The mechanism of acute poisoning involves absorption of products arising from neutralization of sulfide by surface tissues of the respiratory tract (61). The products formed enter the blood through the membrane of the respiratory tract where they are hydrolyzed, with liberation of hydrogen sulfide. The hydrogen sulfide in the blood is rapidly oxidized by molecular oxygen and reduces the oxidative powers of the haemoglobin. Unoxidized hydrogen sulfide can act upon the central nervous system and either cause paralysis of the respiratory centre (at high levels of hydrogen sulfide) or stimulation of the respiratory centre (at lower levels of hydrogen sulfide) (61).

Humans exposed to sublethal levels of hydrogen sulfide may show symptoms of irritation of the mucous membranes, inflammation of the conjunctiva and cornea and slight gastro-intestinal upset. Constant exposure will cause headache, irritability, insomnia, anorexia, nausea, vomiting and slowing of the heart rate . In the case of farm animals, constant exposure to low levels of hydrogen sulfide may result in reduced performance of the affected animals (34,84,104,117).

Exposure to sublethal levels of hydrogen sulfide followed by apparently complete recovery also can be dangerous. Taiganides and White (123) reported that animals which have been exposed to hydrogen sulfide are very sensitive to pneumonia and other respiratory diseases. Baxter (9) also expressed concern over the less noticeable effects of exposure to low concentrations of manure gases.

2.2 Sources of Hydrogen Sulfide in Anaerobic Manure.

The two most important sources of sulfides (or hydrogen sulfide) in anaerobic manure storages are dissimilatory sulfate reduction, and anaerobic protein degradation. Another possible source could be soluble sulfides introduced with the raw waste. Although no data appear to be available on the amounts of sulfide in manure, the sulfide content of the raw excreta is very likely quite small. Sulfides are produced in large amounts in the rumen of sheep and cattle (66), but rarely is there a detectable odor of hydrogen sulfide from fresh animal excreta. Any small amount of hydrogen sulfide produced in the gut but not assimilated by the gut microflora or by the animal itself would be oxidized quickly upon atmospheric exposure.

2.2.1 Dissimilatory Sulfate Reduction.

The reduction of sulfate, and other inorganic oxidized forms of sulfur, to sulfide is accomplished by plants and a wide variety of microorganisms (37). Assimilatory sulfate reduction refers to the reduction of sulfate with the production of only sufficient sulfide to meet the nutritional requirements of the organism. Plants and most bacteria are capable of only this type of sulfate reduction. A few microorganisms, including a variety of yeasts and a small group of anaerobic bacteria, are capable of dissimilatory sulfate reduction with the production of massive quantities of sulfide. In dissimilatroy sulfate reduction, the organisms use sulfate as the terminal electron acceptor in their energy metabolism (102).

Two genera of bacteria, Desulfovibrio and Desulfotomaculum, are known to be capable of dissimilatory sulfate reduction in the presence of a suitable electron donor (107). Some distinctive characteristics and the currently accepted names of known species of both genera are given in Appendix A.

Desulfovibrio desulfuricans is the prototype species of dissimilatory sulfate reducers. Suitable electron donors (oxidizable substrates) for D. desulfuricans include various simple carbohydrates, organic acids, alcohols and amino acids (121). They cannot oxidize cellulose but can develop on organic acids produced by anaerobic cellulose-decomposing bacteria. In addition to sulfate, suitable electron acceptors for D. desulfuricans are hyposulfite, metabisulfide, tetrathionate, sulfite and thiosulfate (121). Dithionate, peridsulfate, formaldehyde-sulfoxylate, sulfamate, benzene sulfonate, methanesulfonate, β-hydroxy-ethane sulfonite, sodium thylsulfate, dimethylsulfone, and cystine can not be reduced by Desulfovibrio.

An example of the energy metabolism of Desulfovibrio was given by Decker et al. (35) in which lactate and pyruvate are oxidized to acetate with the concomitant reduction of sulfate to sulfide:

$$2\ \text{lactate} + SO_4^{=} \rightarrow 2\ \text{acetate} + 2HCO_3^{-} + H_2S$$

$$G_0' = -40.6\ \text{Kcal}$$

$$4\ \text{pyruvate} + SO_4^{=} \rightarrow 4\ \text{acetate} + 4HCO_3^{-} + H_2S + 2H^{+}$$

$$G_0' = -85.2\ \text{Kcal}$$

The eight electrons required for the reduction of $SO_4^=$ to $S^=$ are provided by dehydrogenation of the organic substrate. The formation of acetate from lactate and pyruvate results in the formation of 2 ATP (adenosine triphosphate)/mole of reduced $SO_4^=$ and 4 ATP/mole of reduced $SO_4^=$, respectively.

The mechanism of dissimilatory sulfate reduction has been elucidated fairly clearly over the past few years and resembles, in many respects, the more common assimilatory sulfate reduction (35). In the first stage of the pathway, sulfate is activated by an esterification reaction with ATP to form adenosine 5'-phosphosulfate (APS) and pyrophosphate (PP). The reaction is catalyzed by the enzyme ATP-sulfurylase which requires Mg^{++} for activity. Since the equilibrium of the reaction favours the state of ATP and $SO_4^=$, the reaction must be pulled in the direction of APS formation by the hydrolysis of pyrophosphate, the hydrolysis being catalyzed by pyrophosphatase.

$$ATP + SO_4 \rightleftharpoons APS + PP$$

$$PP + H_2O \rightarrow 2P$$

APS then is reduced directly to sulfite and adenosine monophosphate (AMP). The reduction reaction is catalyzed by the enzyme APS reductase.

$$APS + 2e^- \rightleftharpoons AMP + SO_3$$

Sulfite subsequently is reduced further to sulfide by a yet unknown pathway.

$$SO_3^= \rightarrow S^=$$

2.2.2 Anaerobic Protein Degradation.

Hydrogen sulfide may be produced under anaerobic conditions even in the absence of sulfate-reducing bacteria. Both chemical and enzyme-facilitated bacterial transformations have been implicated.

The hydrogen sulfide emanating from volcanoes and hot sulfur springs has a non-biogenic source (33). Gruenwedel and Patnaik (53) presented data to suggest that the production of hydrogen sulfide and methyl mercaptans in canned foods is the result of pyridoxal-metal ion catalyzed decomposition of sulfur-containing amino acids. The high temperature and pressure requirements, however, would seem to exclude pyrolytic decomposition of organic sulfur compounds as a source of hydrogen sulfide in liquid manure storages.

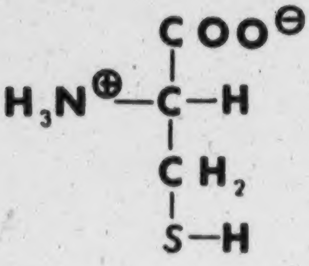
About 1 percent of all plant material and about 2 percent of plant protein are composed of sulfur (109), mostly in the form of the sulfur-containing amino acids (Figure 2). Cysteine (and cystine) and methionine can be degraded enzymatically to, among other compounds, organic acids, ammonia, amines, hydrogen sulfide and mercaptans by heterotrophic bacteria in a process commonly termed putrefaction. Included in this group of bacteria are a large number belonging to the genus Proteus (21) and perhaps some of the sulfate-reducing bacteria previously mentioned. An example of the production of hydrogen sulfide by amino acid degradation is given below in which cysteine is degraded to pyruvic acid, hydrogen sulfide and ammonia (109):

$$CH_2.SH.CHNH_2.COOH + H_2 \rightarrow CH_3.CO.COOH + H_2S + NH_3$$

2.2.3 Relative Importance of each Source of Sulfide.

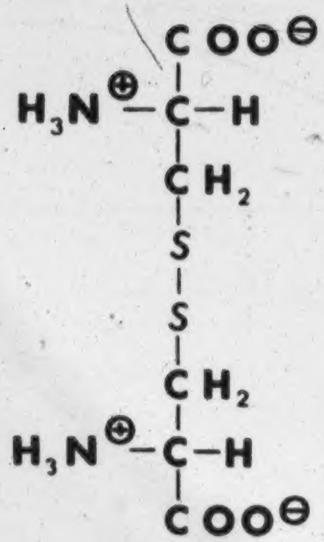
The question of the relative importance of anaerobic protein degradation versus dissimilatory sulfate reduction as sources of hydrogen sulfide in anaerobically fermented manure has received little direct attention. Since the first observation of the occurrence of hydrogen sulfide in the course of anaerobic fermentation of cellulose

L-cysteine



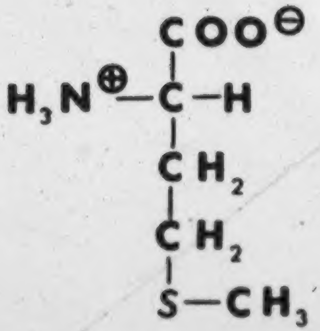
$H_3N^{\oplus}-CH(COO^{\ominus})-CH_2-S-H$

L-cystine



$^{\ominus}OOC-CH(N^{\oplus}H_3)-CH_2-S-S-CH_2-CH(N^{\oplus}H_3)-COO^{\ominus}$

L-methionine



$H_3N^{\oplus}-CH(COO^{\ominus})-CH_2-CH_2-S-CH_3$

Figure 2. Sulfur-containing amino acids.

in 1886 (49), comparatively little work has been undertaken to isolate from anaerobic digestors the bacteria, or other agents, responsible for hydrogen sulfide production.

In 1924, Hotchkiss (65) enumerated organisms responsible for hydrogen sulfide production in a sewage treatment plant. He concluded that sulfate reducers were present in small numbers and that organisms capable of protein degradation were dominant. Aulenbach and Heukelekian (6) provided further evidence of hydrogen sulfide production by degradation of sulfur-containing amino acids, in their studies on the anaerobic treatment of sewage sludge.

Butlin et al. (22) demonstrated the presence of sulfate reducers in sewage sludge, and attempted to enrich these organisms by the addition of sulfate to the raw sewage. They also showed that D. desulfuricans was incapable of growth in sterilized sewage sludge, indicating its dependence on other organisms for the breakdown of the more complex constituents to simple compounds that could then be used.

Torien et al. (125) reported that sulfate-reducing bacteria occurred in raw sewage sludge in numbers exceeding 3 x 10^4/ml. All species isolated proved to be D. desulfuricans, there being no evidence of the presence of the spore-forming Desulfotomaculum. In a more recent publication (124), five to six percent of the bacteria present in an anaerobic digestor were reported to have been capable of hydrogen sulfide production.

Lawrence et al. (72) suggested that sulfate salts, by the action of sulfate-reducing bacteria probably would be the major precursors of sulfides in most industrial wastes. Gloyna and Espino (50) suggested that sulfate-reducing bacteria are responsible for most of the sulfide production in domestic sewage lagoons.

Only one reference (19) to the isolation of sulfate reducers from anaerobically fermented animal manure could be found in the literature. In that report, Desulfovibrio were isolated, probably for the first time, from liquid poultry manure in numbers up to 10^7/gram dry weight of manure. The author suggested that other genera of sulfate-reducing bacteria very likely were present as well. Sulfate-reducing bacteria in manure storage facilities could possibly originate from the soil (11).

Burnett and Dondero (19), in reporting the numbers of sulfate-reducing bacteria present in liquid poultry manure, noted that the peak in numbers of sulfate reducers isolated did not coincide even closely with the peak measured in soluble sulfides. An examination of the published data reveals that the numbers of sulfate reducers and the rate of increase in soluble sulfides also are not correlated, suggesting another numerically more important source of sulfides. The authors proposed that the bulk of the sulfide was produced by saprophytic bacteria which degrade sulfur-containing organic compounds to form hydrogen sulfide.

2.2.4 Influence of the Sulfur Status of Manure on Hydrogen Sulfide Production.

Whether sulfate reduction or anaerobic protein degradation occurs during anaerobic fermentation of manure, and the extent to which each occurs, depends on the composition of the waste. Sulfate reduction can not occur unless the media contains sulfates in sufficient concentration to support the activity of sulfate-reducing bacteria. Similarly, organic sulfur compounds are needed to support those bacteria which produce hydrogen sulfide by protein degradation. The sulfur composition of the manure is clearly the major factor determining the extent of hydrogen sulfide production by either group of bacteria.

An extensive search of the literature provided little insight into the sulfur status of either fresh or fermented manure. Most of the reports which were reviewed dealt with the excretion of sulfur by sheep (8,13,17,18,57,69,70,127) and cattle (57,58,68). Reports on sulfur excretion by pigs were concerned primarily with the effects of sulfate supplementation of the diet on sulfur and nitrogen utilization (71).

The data reviewed on sulfur excreted by ruminants support the following relationships:

1. Sulfur is excreted primarily in three forms (12):
   (a) inorganic sulfate sulfur;
   (b) sulfate esters, usually of carbohydrates, phenols and phenolic steroids (39);
   (c) neutral sulfur, or sulfur bound in a C - S linkage.
2. Sulfur excreted in the feces is a measure of the amount of sulfur that is not absorbed into the blood stream. Sulfur excreted in the urine is a measure of the amount of sulfur that is absorbed but not retained by the body (69).
3. Fecal output of sulfur is related to dry matter intake and is not appreciably affected by increasing or decreasing sulfur contents in the feed eaten. Urinary output of sulfur is

directly related to the concentration of sulfur in the feed eaten (8,18,127).

4. Most fecal sulfur is in the form of neutral sulfur. Most urinary sulfur is in the form of sulfate sulfur (13,18,57).

5. Sulfur excretion is affected by the form of sulfur in the feed eaten (13,69).

One report was located in the literature on sulfur transformations occurring in manure during aerobic storage (95). Feces of chickens, cows, pigs, goats and horses which were incubated aerobically contained appreciably larger quantities of soluble sulfates after incubation than before incubation. Swine feces contained more sulfur than bovine feces but considerably less than chicken feces. A very high degree of correlation ($r = 0.964$) between total sulfur and total nitrogen was reported suggesting that both are mineralized at approximately the same rate. No information on sulfur transformations occurring during anaerobic fermentation could be found.

2.3 Properties of Hydrogen Sulfide in Anaerobic Manure.

2.3.1 Forms of Soluble Sulfides.

Soluble sulfides may exist in anaerobic aqueous media as dissolved hydrogen sulfide (H_2S_{aq}), bisulfide ions (HS^-) and sulfide ions ($S^=$). These three forms are collectively termed total soluble sulfides (T.S.S.). An equation linking the forms of soluble sulfides is given below in terms of the concentrations[a] of each:

$$[T.S.S.] = [H_2S_{aq}] + [HS^-] + [S^=] \qquad (1)$$

---

[a] Square brackets are used throughout this discussion to denote "the concentration of" the bracketed parameter.

In aqueous solution, the weak acid, H_2S_{aq}, is partially ionized to H^+ and HS^-.

$$H_2S_{aq} \rightleftharpoons H^+ + HS^- \tag{2}$$

Further ionization of HS^- yields $S^=$ and an additional H^+.

$$HS^- \rightleftharpoons H^+ + S^= \tag{3}$$

The tendencies for H_2S_{aq} and HS^- to dissociate are given by their respective dissociation constants, K_1 and K_2, where

$$K_1 = \frac{[H^+][HS^-]}{[H_2S_{aq}]} \tag{4a}$$

$$K_2 = \frac{[H^+][S^=]}{[HS^-]} \tag{4b}$$

Values for K_1 and K_2 and their respective logarithmic transformations, pK_1 and pK_2, are given in Table 2.

TABLE 2: DISSOCIATION CONSTANTS FOR HYDROGEN SULFIDE IN AQUEOUS SOLUTION (27).

Reaction	K	pK
$H_2S \rightarrow HS^- + H^+$	9.1×10^{-8}	7.04
$HS^- \rightarrow S^= + H^+$	1.1×10^{-12}	11.96

The equilibrium existing between the three forms of soluble sulfides is very dependent upon the pH of the media. The ratios of the concentration of each form of sulfide to the concentration of total soluble sulfides may be derived as follows:

From equation 1,

$$\frac{[H_2S_{aq}]}{[T.S.S.]} = \frac{1}{1+\frac{[HS^-]}{[H_2S_{aq}]}+\frac{[S^=]}{[H_2S_{aq}]}} \tag{5a}$$

$$\frac{[HS^-]}{[T.S.S.]} = \frac{1}{1+\frac{[H_2S_{aq}]}{[HS^-]}+\frac{[S^=]}{[HS^-]}} \tag{5b}$$

$$\frac{[S^=]}{[T.S.S.]} = \frac{1}{1+\frac{[H_2S_{aq}]}{[S^=]}+\frac{[HS^-]}{[S^=]}} \tag{5c}$$

Rewriting the right hand side of each equation in terms of the dissociation constants, K_1 and K_2 from equation 4,

$$\frac{[H_2S_{aq}]}{[T.S.S.]} = \frac{1}{1+\frac{K_1}{[H^+]}+\frac{K_1K_2}{[H^+]^2}} \tag{6a}$$

$$\frac{[HS^-]}{[T.S.S.]} = \frac{1}{1+\frac{[H^+]}{K_1}+\frac{K_2}{[H^+]}} \tag{6b}$$

$$\frac{[S^=]}{[T.S.S.]} = \frac{1}{1+\frac{[H^+]^2}{K_1K_2}+\frac{[H^+]}{K_2}} \tag{6c}$$

Equations 6a, 6b and 6c are plotted in Figure 3, with pH as the independent variable and at a temperature of 18°C. As indicated by the plotted curves, the equilibrium concentrations of each of the three forms of sulfide change rapidly with pH. At pH = 8, less than 10 percent of the total soluble sulfides exist as dissolved hydrogen sulfide while at pH = 6, more than 90 percent of the total soluble sulfides are in the form of dissolved hydrogen sulfide. At $pH = pK_1 = 7$, the concentration of dissolved hydrogen sulfide and of bisulfide are equal, and at $pH = pK_2 = 12$, the concentration of bisulfide and sulfide are equal.

2.3.2 Desorption of Dissolved Hydrogen Sulfide.

Desorption of dissolved hydrogen sulfide results in an accumulation of gaseous hydrogen sulfide (H_2S_g) above a sulfide-containing manure solution. The equilibrium concentration of H_2S_g is given by Henry's Law[a] in terms of an absorption coefficient, α, and the concentration of dissolved hydrogen sulfide (72).

$$[H_2S_g] = \frac{1}{\alpha}[H_2S_{aq}]$$

Values for α at different temperatures are given in Table 3.

---

[a] According to Henry's Law (32), the concentration A* of dissolved gas in equilibrium with a partial pressure of Pi of the gas, is given by Pi = HeA*, where He is the "Henry's Law Constant". The reciprical of He may be written as α, the absorption coefficient.

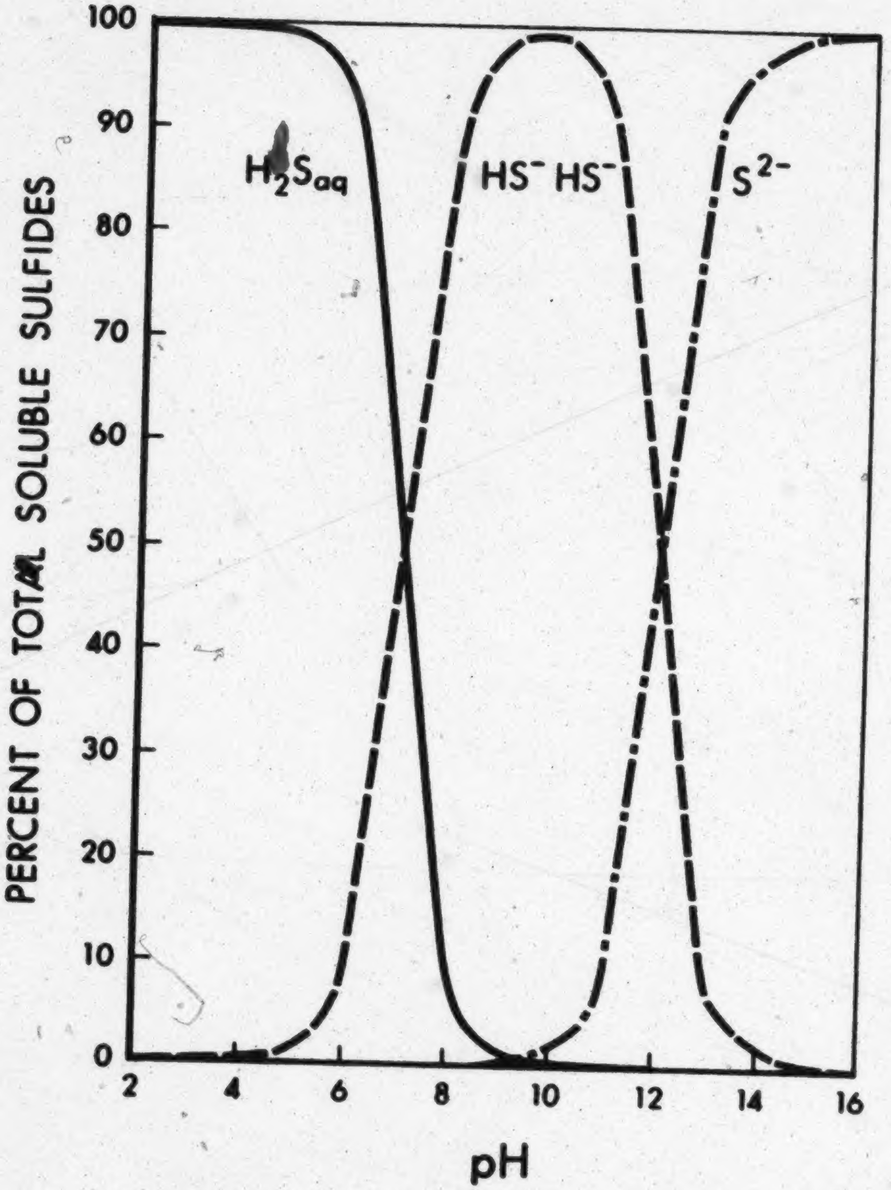


Figure 3. Forms of soluble sulfides in aqueous solution at 18°C.

TABLE 3: SULFIDE EQUILIBRIUM CONSTANTS AT VARIOUS TEMPERATURES (72).

Temperature (^oC)	Ionization Constant K_1	Absorption Coefficient α
18	9.1×10^{-8}	2.72
25	11.2×10^{-8}	2.28
35	14.9×10^{-8}	1.83
45	19.4×10^{-8}	1.52

The equilibrium concentration of H_2S_g clearly will be influenced by any factors that cause a change either in α or $[H_2S_{aq}]$. The most important of these factors are pH and temperature. The relationship between the pH of a sulfide-containing solution and the concentration of H_2S_{aq} has been discussed in the previous section. Since the concentration of H_2S_g is directly proportional to the concentration of H_2S_{aq}, more hydrogen sulfide would be expected to be evolved from a manure solution with a lower pH than from a manure solution with a higher pH value.

The effect of temperature on the desorption of hydrogen sulfide is more obscure. As shown in Table 3, α decreases as the temperature increases at the rate of about 2 percent per ^oC change in temperature over the range of 18 to 45^oC. This relationship is confirmed by the observation that the solubility of hydrogen sulfide in water decreases from 437 cm^3/100cc at 0^oC to 186 cm^3/100cc at 40^oC (27). However, because of the dependence of K_1 on temperature (Table 3), the equilibrium concentration of H_2S_{aq} decreases with increasing temperature. Of these two influences, that of a decreasing α (decreasing solubility) with increasing temperature is greater. Consequently, the concentration of H_2S_g would be expected to increase with an increase in temperature, given the same concentration of total soluble sulfides in the manure solution.

Up to this point, mention only has been made of the equilibrium concentration of H_2S_g associated with a manure solution. However, given the situation where sulfides are rapidly being produced, equilibrium may not be established between the concentrations of hydrogen sulfide in the gaseous and dissolved forms. Under such conditions, the rate of desorption becomes the controlling factor over the instantaneous concentration of H_2S_g.

Neglecting the effect of desorption on the temperature at the gas-liquid interface, and assuming that the concentration of dissolved gas is uniform throughout the body of liquid (i.e., diffusion of the gas to the surface is not the rate-limiting process), the rate of desorption of a gas from solution is proportional to the driving force for desorption and the interfacial area for desorption (32). The driving force is essentially the concentration gradient between the instantaneous and equilibrium concentrations of hydrogen sulfide. The effective interfacial area of desorption is clearly a function of the liquid surface conditions. For example, during quiescent storage, the build-up of a scum layer may reduce the rate of transfer of hydrogen sulfide from a manure solution by making a portion of the surface "impermeable" to gaseous exchange. On the contrary, agitation and mixing during fermentation likely increases the effective interfacial area and hence, may enhance the desorption of hydrogen sulfide.

2.3.3 Effect of Sulfides on the Anaerobic Digestion Process.

The deleterious effect of high concentrations of soluble sulfides in anaerobic digestors has been reported by several researchers. Butlin et al. (22) found that soluble sulfides at 200 mg/l totally inhibited methane formation in semicontinuous fermentation; lesser concentrations of sulfides decreased gas production initially but there was a slow recovery to normal, suggesting acclimatization of the bacteria.

Lawrence et al. (72) also reported cessation of gas production when the level of soluble sulfides exceeded 200 mg/l as S. Gas production was affected first, followed by an accumulation of volatile acids, suggesting that the acid-forming bacteria involved in the methane digestion process are affected before the methane formers. Insoluble sulfides at concentrations of 400 mg/l as S had no effect on anaerobic treatment.

The bacteria which produce hydrogen sulfide themselves are inhibited by high sulfide concentrations. Despite the fact that these organisms have a remarkable tolerance for hydrogen sulfide, there is above which the sulfide is toxic or at least inhibitory to them. The minimum inhibitory concentration of hydrogen sulfide for sulfate reducers is thought to be about 2500 ppm (87,115), but much lower concentrations have been reported to inhibit growth (85,112). The toxicity of sulfides to sulfate reducers may account for the observed linear growth curve of these organisms (107).

2.4 Control of Hydrogen Sulfide from Anaerobic Manure.

The biological and chemical reactions that ultimately result in the presence of hydrogen sulfide gas in the atmosphere surrounding anaerobically fermented manure are summarized in Figure 4. Selective control could be exerted on key reactions in the system to:

(1) minimize the concentration of dissolved hydrogen sulfide;
(2) minimize the desorption of dissolved hydrogen sulfide; or
(3) minimize the amount of gaseous hydrogen sulfide which can escape from the area immediately surrounding the manure into the area of animal or human occupancy.

Control at any one of these three stages in the system would eliminate the nuisance conditions associated with hydrogen sulfide from animal manure. In the sections that follow, each alternative is examined critically on the basis of theoretical relationships and practical experiences reported in the literature. A flow sheet outlining the various alternative control measures is presented in Figure 5.

2.4.1 Minimize the Concentration of Dissolved Hydrogen Sulfide.

As discussed earlier (Section 2.3.2), the equilibrium concentration of gaseous hydrogen sulfide associated with a sulfide-containing aqueous media is directly proportional to the concentration of dissolved hydrogen sulfide in the media. If the concentration of dissolved hydrogen sulfide could be kept to a minimum, the amount of gaseous hydrogen sulfide released from solution also would be minimized. Two alternatives appear to exist by which the objective of minimization of dissolved hydrogen sulfide could be achieved, namely,

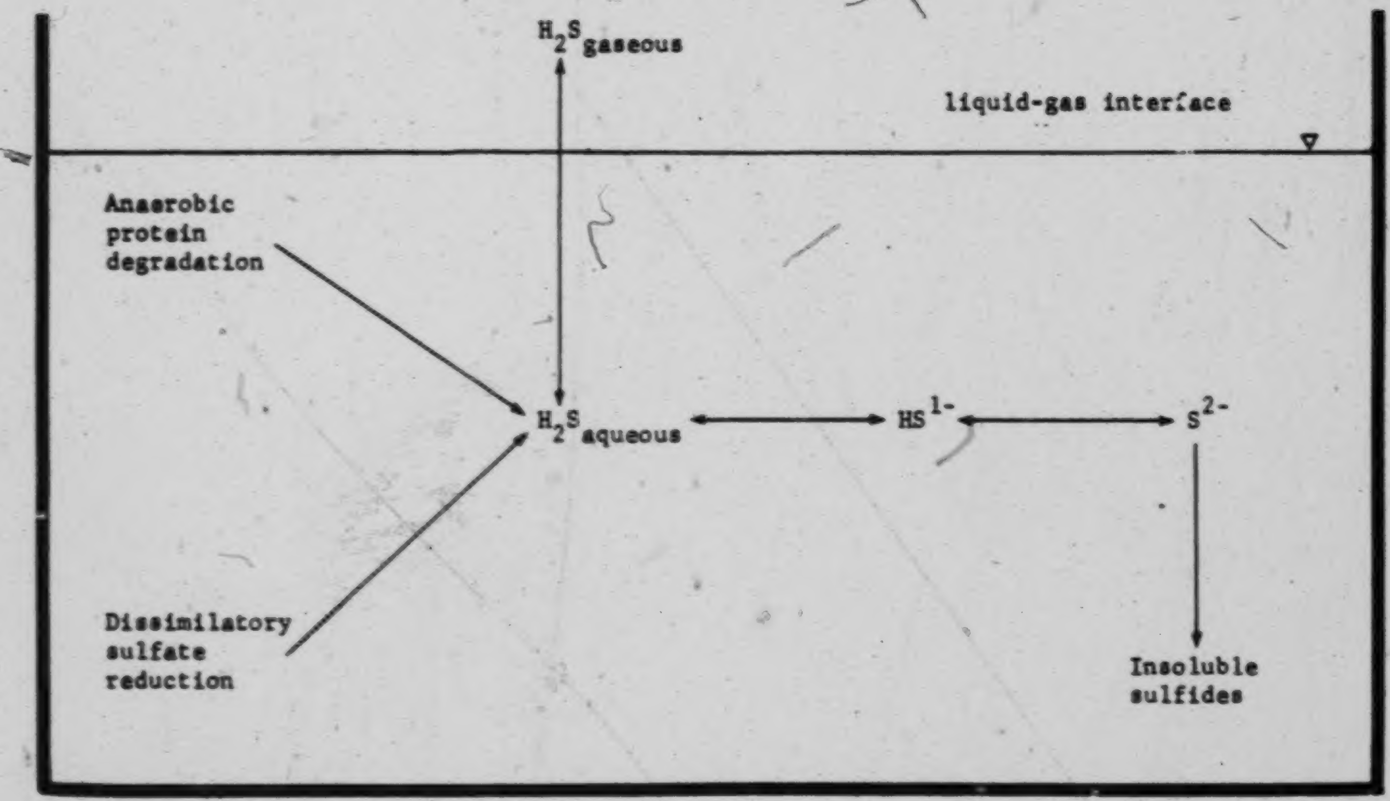

$H_2S_{gaseous}$
liquid-gas interface
Anaerobic protein degradation
$H_2S_{aqueous}$
HS^{1-}
S^{2-}
Dissimilatory sulfate reduction
Insoluble sulfides

Figure 4. Chemical and biological reactions involving sulfur in anaerobic manure.

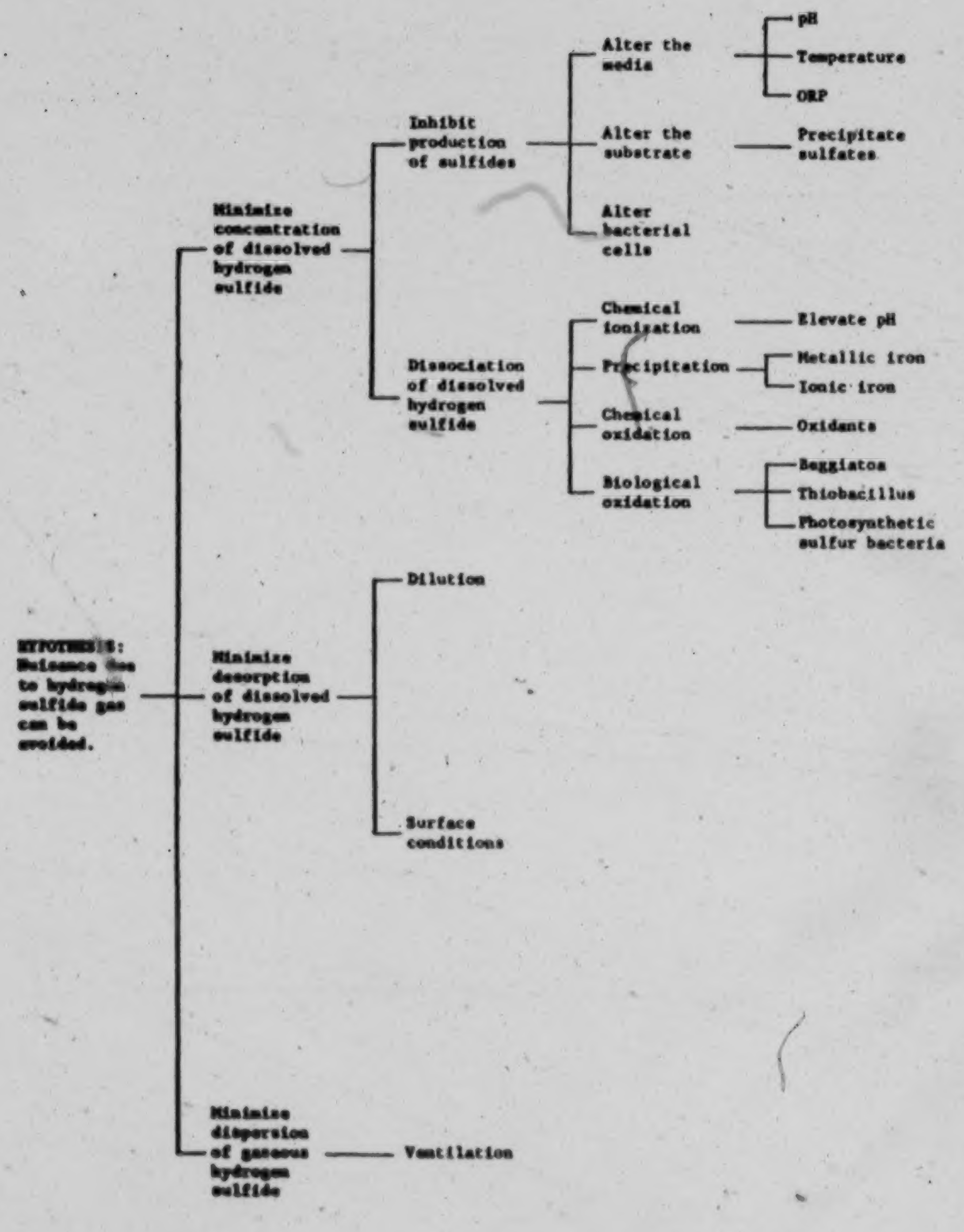

HYPOTHESIS: Nuisance due to hydrogen sulfide gas can be avoided.
Minimize concentration of dissolved hydrogen sulfide
Inhibit production of sulfides
Alter the media
pH
Temperature
ORP
Alter the substrate
Precipitate sulfates
Alter bacterial cells
Dissociation of dissolved hydrogen sulfide
Chemical ionization
Elevate pH
Precipitation
Metallic iron
Ionic iron
Chemical oxidation
Oxidants
Biological oxidation
Beggiatoa
Thiobacillus
Photosynthetic sulfur bacteria
Minimize desorption of dissolved hydrogen sulfide
Dilution
Surface conditions
Minimize dispersion of gaseous hydrogen sulfide
Ventilation

Figure 5. Control of hydrogen sulfide from anaerobic manure.

inhibition of the production of soluble sulfides and dissociation of dissolved hydrogen sulfide to less objectionable forms of sulfur.

2.4.1.1 Inhibition of Hydrogen Sulfide Production.

A large array of physical and chemical agents have a potential ability to inhibit the production of hydrogen sulfide by destroying, or at least reducing the activity of, the bacteria which are responsible for its production. These bacteria, hereafter termed the target organisms, produce hydrogen sulfide either by dissimilatory sulfate reduction or by anaerobic protein degradation.

The effectiveness of a potential inhibitor, be it chemical, physical or biological, will depend upon its ability to either create or maintain an environment which is unfavourable to the target organisms. The ideal inhibitor also should have the following characteristics:

1. If a chemical is used, that chemical should not be harmful or toxic to animals and operators at the concentrations being considered.
2. If a chemical is used, it should be totally consumed or converted to products which will not affect adversely soil microorganisms if the treated waste is to be disposed of by field spreading, or otherwise create an ecological hazard.
3. The inhibitor should not exert any undesireable side-effects such as the production of precipitates, chemical complexes or gaseous emmissions which are toxic, potentially dangerous, or difficult to dispose of and to handle.

4. The inhibitor should affect only the target organisms and not those which are involved in the biodegradation and liquefication of the manure organics. In general, this criterion may be unnecessarily restrictive and may not be too important.
5. The inhibitory agent should be readily available, economical to use, and easy to apply.

For convenience in the ensuing discussion, inhibitors will be classified according to their specific mode of action:

1. Alteration of bacterial cells and metabolic processes: Chemical or physical agents may be applied to the media that will cause damage to cellular components and/or interfere with normal metabolic functions. Direct physical contact between the inhibitor and the target organisms is necessary.
2. Alteration of the substrate: Material entering the culture vessel may be treated to remove or render unavailable a substrate which is critical to the growth and/or reproduction of the target organisms.
3. Alteration of the media: The physio-chemical properties of the media may be altered beyond the tolerances of the target organisms.

(1) Alteration of bacterial cells and metabolic processes:

Most of the research that has been reported on the inhibition of hydrogen sulfide production has been concerned exclusively with sulfate-reducing bacteria. The petroleum and natural gas industries have been especially active in this area in an effort to combat the serious problems created by the production of hydrogen sulfide in oil and gas aquifers and in underground storage tanks (33).

Details are given in Table 4 on seven categories of bacterial agents, all of which have been used against sulfate-reducing bacteria. The results of research and experience referred to in the table support the following conclusions:

(a) All of the agents except mercurials are effective against laboratory cultures of sulfate-reducing bacteria, albeit at very high concentrations of the compound in some cases. Mercurials are generally ineffective, probably as a result of their deactivation by precipitation as insoluble mercuric sulfide (115).

(b) The effectiveness of several of the inhibitors is very temperature dependent (115).

(c) Various strains and species of sulfate-reducing bacteria respond differently to chemical inhibitors. The sporulating species are generally more resistant than the non-sporulating species (114). Furthermore, mixed cultures respond differently than pure cultures to chemical inhibition; for example, *Pseudomonas aeruginosa* and *D. desulfuricans* react differently to chemical inhibition when each is considered alone than when they exist together in a mixed culture (10). Such results indicate the unreliability of extrapolating controlled laboratory results to uncontrolled field situations.

(d) In the few cases where field investigations have been conducted, inhibitors were not as effective as they had been in laboratory trials. Pankhurst (99) suggested that flavin dyes, phenolics,

TABLE 4: BACTERIAL INHIBITORS THAT HAVE BEEN USED AGAINST SULFATE-REDUCING BACTERIA.

Category	Principle Mode of Action (47,115)	Examples
Antibiotics	(a) Inhibition of protein biosynthesis	(a) Streptomycin Chloramphericol Tetracycline (115)
	(b) Interference with murein biosysthesis	(b) Penicillin (115)
	(c) Interference with the function of the semi-permeable membrane	(c) Polymyxin (115)
Quaternary Ammonium Compounds (Detergents)	Surface-active agents; interfere with the semi-permeable membrane causing leakage of cell constituents and cytolytic damage; enzyme proteins are also damaged.	alkylbenzyl trimethyl ammonium chloride (60) "Arquad" Cetyltrimethyl-ammonium bromide (33,99,115)
Dyes	Direct toxins	Genetian violet (99,115) Acridine dyes (85,115)
Mercurials	Inhibition of SH enzyme action	chloromercuriphenol phenyl mercurics mercuric chloride (115)
Ultraviolet irradiation	Physical disruption of the cellular structure	10 minute exposure to U.V. light (2537A) 36 inches distant at an intensity of 44.5 µwatt/cm^2 (115)
Sulfate Analogs	Interfere with enzyme systems involving intercellular transport and reduction of sulfate by sulfate-reducing bacteria	chromate (38,99,111) molybdate (111) tungstate (111)
Phenolic Substances	Denaturation of proteins; effectiveness is increased by the addition of halogen groups to the phenolic compound	phenol (115) tannin (15,115) poly-chlorinated phenols (33, 99,115)

and quaternary ammonium compounds are deactivated by suspended organics in the media. The same is probably true of sterilization by ultraviolet irradiation.

(e) All but the sulfate analogs are broad-spectrum antibacterial agents, affecting most of the bacteria in the culture media. Since the target organisms represent such a small percentage of the total bacterial population in field situations, large quantities of the inhibitors in a sense are "wasted" when they are applied at bacteriocidal concentrations. Sulfate analogs are specific for sulfate-reducing bacteria, are not always effective against even these bacteria, and are totally ineffective against other groups of bacteria including those producing hydrogen sulfide by anaerobic protein degradation.

(f) The results of batch-culture trials should not be extrapolated unconditionally to larger-scale continuous-culture systems. Because of the very short generation time, and because of the relatively high frequency of mutations, bacteria are capable of developing resistance to inhibitors. Zablatzky (133) has reviewed the theory of bacterial acclimatization and has warned about the misinterpretations which can arise by not properly considering this phenomenon in inhibition studies.

These conclusions suggest that the chemical and physical agents listed in Table 4 are of doubtful value as inhibitors of hydrogen sulfide production from manure.

(2) Alteration of the Substrate:

In a report dealing with the production of hydrogen sulfide gas from sewage sludge, Pandit (98) suggested that the evolution of the gas could be reduced by precipitating sulfates from the raw sewage as insoluble calcium sulfate. Pankhurst (101) reported the removal of sulfates from gas holding-tank waters by precipitation as barium sulfate. Santry (116) has shown that sulfide production from sewage sludge is a direct function of the concentration of sulfate in the sludge, and that the possibility of sulfide generation is removed under certain supporting conditions when the concentration of sulfate is less than 25 mg/l.

All of these reports indicate that the production of hydrogen sulfide gas from fermenting organic matter may be controlled by controlling the sulfur composition of the waste. Information is needed on the sulfur status of animal manures to allow an evaluation of this method of hydrogen sulfide control; however, such information does not appear to be available.

(3) Alteration of the Media:

Although microorganisms have a unique ability to adapt to almost all environmental conditions, extremes in the physio-chemical properties of the culture media may be bacteriocidal or bacteriostatic under certain conditions. Aside from the nutrient composition, the three most important properties of a media affecting growth of microorganisms are pH, temperature and the the oxidation-reduction potential.

(a) pH: One of the early attempts to inhibit sulfate-reducing bacteria involved lowering the pH of the media to below pH = 5 by the addition of sulfuric acid (20). A pH of 3.4 was observed to give good control of sulfate-reducing bacteria in oil well flooding systems and in high sulfate ponds (115).

Santry (116) reported that the generation of hydrogen sulfide gas from sewage sludge is greatest at pH values of 7.5 to 8.0 and declines with both increasing and decreasing pH. In principle then, both large increases and large decreases in pH should inhibit the production of hydrogen sulfide. Such has not been found always to be the case. Tuttle et al. (126) were able to isolate a species of sulfate-reducing bacteria which was active at a pH of 3.0, while Pankhurst (100) reported that certain species of sulfate reducers can survive up to a pH of 11.7, and become active when the pH drops. No doubt, spore-forming species of bacteria may be able to survive over a wide range of pH values so that pH control might not be expected to provide absolute control over the production of hydrogen sulfide in manure.

Numerous reports can be found in the literature indicating success with lime for odor control in domestic water and wastewater treatment plants (120). Some experience also has been recorded with pH elevation for odor control from manure. Hammond et al. (56) reported that hydrogen sulfide was present in much smaller concentrations in hog manure pits treated with hydrated lime to a pH of 10.0 than in untreated control pits. Experiments with dairy cattle manure also indicated hydrogen sulfide control by liming to a pH of 11 to 12 (128).

Deibel (36), and other researchers cited by Deibel, have attempted to control odors from poultry manure by adjusting the pH of the manure in both directions. Lowering of the pH was accomplished biologically by the addition of glucose which is rapidly fermented by the microflora to organic acids. At a concentration of 1%, glucose additions resulted in a drop in pH to 5.2 within 48 hours. However, odor production during this period was enhanced, thereby negating this approach to odor control. Experiments to raise the pH of the manure by liming indicated that liming abated both bacterial growth and odor for an initial period of 7 - 10 days. After about a week, the pH of limed manure dropped from 10 to between 7 and 8 where it levelled off regardless of the concentration of lime. Liming was considered impractical because of the requirement to stir the manure for proper application of the lime.

(b) Temperature: According to the Van't Hoff Rule, the biological reaction rate doubles for every 10°C rise in temperature over a restricted range. Santry (116) reported that the rate of production of hydrogen sulfide from sewage sludge increases by 7 percent/°C rise in temperature up to 30°C. Chaudhry and Cornfield (26), in agreement with Santry, showed that the activity of sulfate-reducing bacteria declines at very high temperatures (above 30°C). Gloyna and Espino (50) cited experimental evidence for a sharp decrease in sulfide production below 15°C and an approximate doubling of the rate of production for each 10°C rise in temperature above 15°C. This relationship between temperature and biological activity may help to explain the observed differences between the odor intensities of manure during the summer and winter months. Despite the fact that cold temperatures reduce the production of hydrogen sulfide from manure, there appears to be little chance to make use of this relationship on a practical scale.

(c) Oxidation-reduction potential: The degree of anaerobiosis of a body of manure can be measured in terms of its electrode potential (Ecal), where Ecal is the oxidation-reduction potential (ORP) measured with a platinum electrode and a saturated calomel electrode (30). The ORP is an indication of the oxidizing or reducing powers of the media. A highly negative Ecal (or ORP) value is characteristic of anaerobic conditions whereas a positive Ecal value indicates aerobic conditions. The ranges of Ecal over which aerobic, facultative and anaerobic bacteria may operate are +400 to -200 mv, +50 to -100mv, and +50 to -420 mv, respectively (30). The bacteria which produce hydrogen sulfide are all anaerobes and, in the case of sulfate reducers, have been shown to require an ORP of -200 mv for optimal activity.

Since the bacteria which produce hydrogen sulfide are inactive, or at best slowly active, at elevated ORP values, hydrogen sulfide production in manure may be inhibited by preventing the lowering of the ORP of the manure to a level which is favoruable to anaerobic bacteria. The maintenance of an elevated ORP value would require the aid of a suitable oxidizing agent since aerobic and facultative bacteria will utilize continuously all available oxygen in the media.

Almost all of the research to date on ORP control in livestock manure has considered air as the oxidizing agent. Mechanical, pneumatic and hydraulic aerators have been utilized to supply air to the manure. In general, aeration has been very successful in controlling not only hydrogen sulfide but most other toxic and malodorous compounds as well. Furthermore, a high degree of organics stabilization is achieved by aerobic treatment (89,92,132)

Despite the effectiveness of aerobic treatment, however, all of the currently available methods of aeration suffer from several disadvantages, perhaps the greatest of which are unreliable cold weather operation and high costs (106). In an effort to reduce the costs of aerobic treatment, recent research has been aimed at minimum aeration techniques in which only sufficient air is supplied to maintain odorless conditions (30,75,94,97,105). This research has demonstrated that odor control can be achieved without maintaining residual dissolved oxygen in the manure. These new methods of aeration will require further research and development before aerobic treatment can be considered as a practical means of odor control where waste treatment is not the major criterion for requiring aeration.

Aeration is not the only means by which control can be exerted over the ORP of manure. Several chemical oxidizing agents have been reported as being effective for control of odors arising from organic waste fermentation. Strong chemical oxidizing agents will actually exert an inhibitory effect on the release of hydrogen sulfide from manure in three ways. Firstly, the oxidizing agent will increase the ORP of the manure with much the same effect as aeration. Secondly, sulfide present in the manure would be expected to be oxidized to elemental sulfur, an effect which will be discussed in a later section. The third control over hydrogen sulfide production involves the direct bactericidal effect that strong oxidizing agents have on all bacteria.

Oxidizing agents used in domestic water and wastewater treatment include ozone, chlorine, potassium permanganate and hydrogen peroxide (44). When added to a wastewater, these agents react with all reducing substances including inorganic Fe^{++}, NO_2^- and H_2S along with most of the organic material. Whereas the reaction with the inorganic compounds proceeds rapidly and stoichiometrically (44), organic compounds react more slowly, the extent of the reaction depending upon the excess of oxidizing agent which is present. Levels of chlorine much smaller than the total chlorine demand (the amount required to totally disinfect the media) have been shown to delay the formation of sulfide from domestic sewage (4), but the quantity of sulfide eventually produced in chlorinated sewage is as great as that in untreated sewage. Clearly then, the primary effect of oxidizing agents added to a media such as manure is the oxidation of reduced inorganic compounds in the media, resulting in a lowering of the ORP, followed by destruction of bacterial cells and other organic matter.

Very little research and experience has been recorded on the application of oxidizing agents to manure for odor control. Chlorination of dilute wastewaters from duck farms is perhaps the only current practical application of chlorination and, in this case, the objective is disinfection rather than odor control (48).

Although not yet developed for practical use, chlorination for control of odor from manure has been the subject of at least three investigations (34,56,67). In these investigations, chlorine added to hog manure substantially reduced the odor of the manure compared to untreated controls. Irgens and Day (67) noted a slight odor of chlorine gas when hog waste was chlorinated with the gas and suggested that this could be harmful to the pigs. These same researchers also presented data on organic matter removals by chlorination which indicated a large resistance to oxidation by some small organic molecules.

Faith (45) evaluated several chemical agents for controlling odors from feedlot manure. A one percent aqueous solution of potassium permanganate applied 3 times a year at the rate of 20 pounds of the chemical per acre was very effective for odor control. Odor development in anaerobic sumps and ditches also was abated effectively by addition of potassium permanganate either as a solid or in water solution. Faith suggested that potassium permanganate oxidized odorous compounds in the manure for rapid odor control followed by alteration of the bacterial population so that putrefying bacteria did not develop. This alteration of the bacterial populations could be due to the change in the ORP of the manure which is brought about by the oxidizing agent.

An oxidizing agent which is only now beginning to receive attention as a potential odor control additive is ammonium persulfate. Initial research conducted in Sweden (74) has shown that this chemical effectively suppresses odors when added to manure just prior to field spreading.

Although not generally recognized as very strong oxidizing agents, nitro-compounds have been reported as effective inhibitors of hydrogen sulfide production. Reports of adding nitrogen fertilizer to septic tanks which had gone 'sour' have been received from time to time. Furthermore, Stone and Kahle (122) reported that sodium nitrate is being used successfully to control odors from lagoons receiving organic wastes from some food processing industries.

Saleh et al. (115) cited two reports in which potassium and ammonium nitrate were shown to be effective inhibitors of sulfate-reducing bacteria at concentrations of 500 to 1000 mg/l as NO_3. Allen (4) showed that nitrobenzene, dinitrobenzene, picric acid and trinitrotoluene (TNT) in concentrations ranging from 2 to 20 ppm effectively delayed the production of sulfide from anaerobically incubated sewage. At high concentrations, nitrobenzene and dinitrobenzene exhibited bacteriocidal effects whereas picric acid and TNT did not. Nitrate-nitrogen inhibited hydrogen sulfide production at 100 to 1000 ppm. The author suggested that the nitro-compounds exhibited inhibitory tendencies by retarding the lowering of the redox potential of the sewage to a region favourable for development of sulfate-reducing anaerobes. This conclusion was supported by evidence that the compounds tested had no effect on either aerobic or facultatively anaerobic organisms. Other research also has shown that the reduction of sulfate levels in waterlogged soil (26,29,43) and in sewage (116) does not occur until all molecular oxygen and oxidized nitrogen compounds have been reduced.

2.4.1.2 Dissociation of Dissolved Hydrogen Sulfide.

Perhaps the most obvious means of minimizing the concentration of dissolved hydrogen sulfide in manure is to inhibit the production of sulfides as discussed in the previous section. Another feasible approach, however, may be to allow the production of hydrogen sulfide but to convert the sulfide produced to non-volatile or otherwise less objectionable forms of sulfur. The restrictions placed on agents used to inhibit hydrogen sulfide production also must be applied to any chemical, physical, or biological agents used to promote dissociation of dissolved hydrogen sulfide.

(1) Chemical Ionization:

As discussed in Section 2.3.1, dissolved hydrogen sulfide is partially ionized to HS^- and $S^=$, the extent of ionization being largely dependent upon the hydrogen ion concentration of the solution. For example, at a pH of 8,less than 10 percent of the total soluble sulfides exist as dissolved hydrogen sulfide (Figure 3). In addition to having a bacteriocidal effect, therefore, liming may reduce the concentration of dissolved hydrogen sulfide by aiding its conversion to innocuous ammonium, sodium and metal sulfides.

(2) Precipitation as Insoluble Metal Sulfides:

The equilibrium concentration of dissolved hydrogen sulfide also can be decreased by precipitating soluble $S^=$ as insoluble metal sulfides. Miller (86,87) found that precipitates of lead, zinc, antimony, bismuth, cobalt, nickel, cadmium and iron could be obtained in culture media where sulfate reduction was occurring. The author noted that removal of hydrogen sulfide by precipitation did not appear to affect the rate of growth of sulfate reducers, but did increase the total amount of sulfide produced. Similar results have been reported by Wainwright (129) who showed that certain trace metals greatly increase the total yield of sulfides by sulfate-reducing species of yeasts. Pandit (98) and Pankhurst (101) have reported that the addition of iron salts to sulfide-containing media effectively prevents the evolution of hydrogen sulfide gas from the media.

Miller (86) pointed out that any metal salts could be toxic to anaerobic bacteria if the cation is soluble and is added in excessive amounts. Furthermore, the anion released may reduce the pH of the medium to toxic levels (87). However, Lawrence et al. (72) indicated that addition of iron as $FeCl_3$ at 1400 mg/l had little effect on digestor efficiency, but effectively precipitated sulfides from the biological environment.

Whereas there would appear to be some disagreement about the effects of soluble metal salts on anaerobic bacteria, the metal sulfides that are precipitated do not appear to have any adverse effects on digestor efficiency. Lawrence et al. (72) and Aulenbach and Heukelekian (6) showed that the bacteria involved in anaerobic digestion are not affected by iron sulfides in the media.

The research reported above suggests that, if large dosages of iron ions can be economically attained, such doses will effectively precipitate sulfides and will not in themselves adversely affect digestor efficiency, nor will the precipitate formed adversely affect digestor efficiency. A more practical approach from the standpoint of acquisition of the additive, however, might involve the use of iron in the form of a powder or larger sheets or bars of metal.

Starkey (121) estimated that 2.5 percent of all steel and iron in service in the United States corrodes away every year, and that corrosion in which sulfate-reducing bacteria are implicated probably accounts for a large percentage of the total. Davis (33) and Pankhurst (101) reported that sulfate-reducing bacteria are responsible for corrosion of oil-well casings and well-head equipment.

Another case of anaerobic corrosion was reported during a larger study involving hydrogen sulfide production from model stabilization ponds (50). In that study, laboratory ponds consisted of iron drums with plastic interior linings. The plastic coating failed on one of the ponds and excessive corrosion occurred. The iron concentration in the affected pond increased to 3.5 mg/l compared to 0.2 to 0.3 mg/l in the other tests, with practically all the sulfides being precipitated as iron sulfide.

The corrosion of metals would be expected to be slight in a neutral and anaerobic media (14). Under chemically neutral conditions, the potential of the metal with respect to the electrolyte will not be in general sufficiently negative to overcome the hydrogen overpotential and hence to allow the evolution of hydrogen gas; rather the tendency will be for the cathode of corrosion cells to become polarized and for corrosion to cease. Under anaerobic conditions, the common alternative cathodic reaction to hydrogen evolution, namely oxidation of hydrogen gas by oxygen, is not available. Neither will alternative oxidizing agents such as ferric ions or peroxide be present in most natural anaerobic environments.

To account for the observed phenomenon of anaerobic corrosion, the theory of Von Wolzogen Kuhr and Van der Vlugt (121) was proposed (Figure 6). According to their theory, sulfate-reducing bacteria increase the rate of corrosion by serving to depolarize the cathode of corrosion cells via hydrogen uptake and to depolarize the anode via a reaction between Fe^{++} and H_2S. The products of corrosion are ferrous sulfide (thereby removing sulfur from solution) and ferrous hydrates, these products persisting in the medium under anaerobic conditions. The reactions involved may be summarized thus (121):

$$\begin{array}{l}
8H_2O \rightleftharpoons 8H^+ + 8\ OH^- \\
4\ Fe^0 + 8H^+ \rightarrow 4\ Fe^{=} + 8H \\
Na_2SO_4 + 8H \rightarrow Na_2S + 4\ H_2) \\
Fe^{=} + Na_2S \rightarrow FeS + 2\ Na^+ \\
3\ Fe^{=} + 6\ OH^- \rightarrow 3\ Fe(OH)_2 \\
\hline
4\ Fe^0 + Na_2SO_4 + 4\ H_2O \rightarrow FeS + 3\ Fe(OH)_2 + 2\ NaOH
\end{array}$$

This mechanism explains the observed phenomenon that the reaction results in an increase in pH.

The theory of Von Wolzogen Kuhr and Van der Vlugt has been challenged because there is no direct conclusive evidence that the coupling of cathodic hydrogen to bacterial sulfate reduction is a requirement for anaerobic bacterial corrosion. From a study of the potential changes of iron in pure bacterial cultures, corrosion could be attributed entirely to the anodic stimulatory

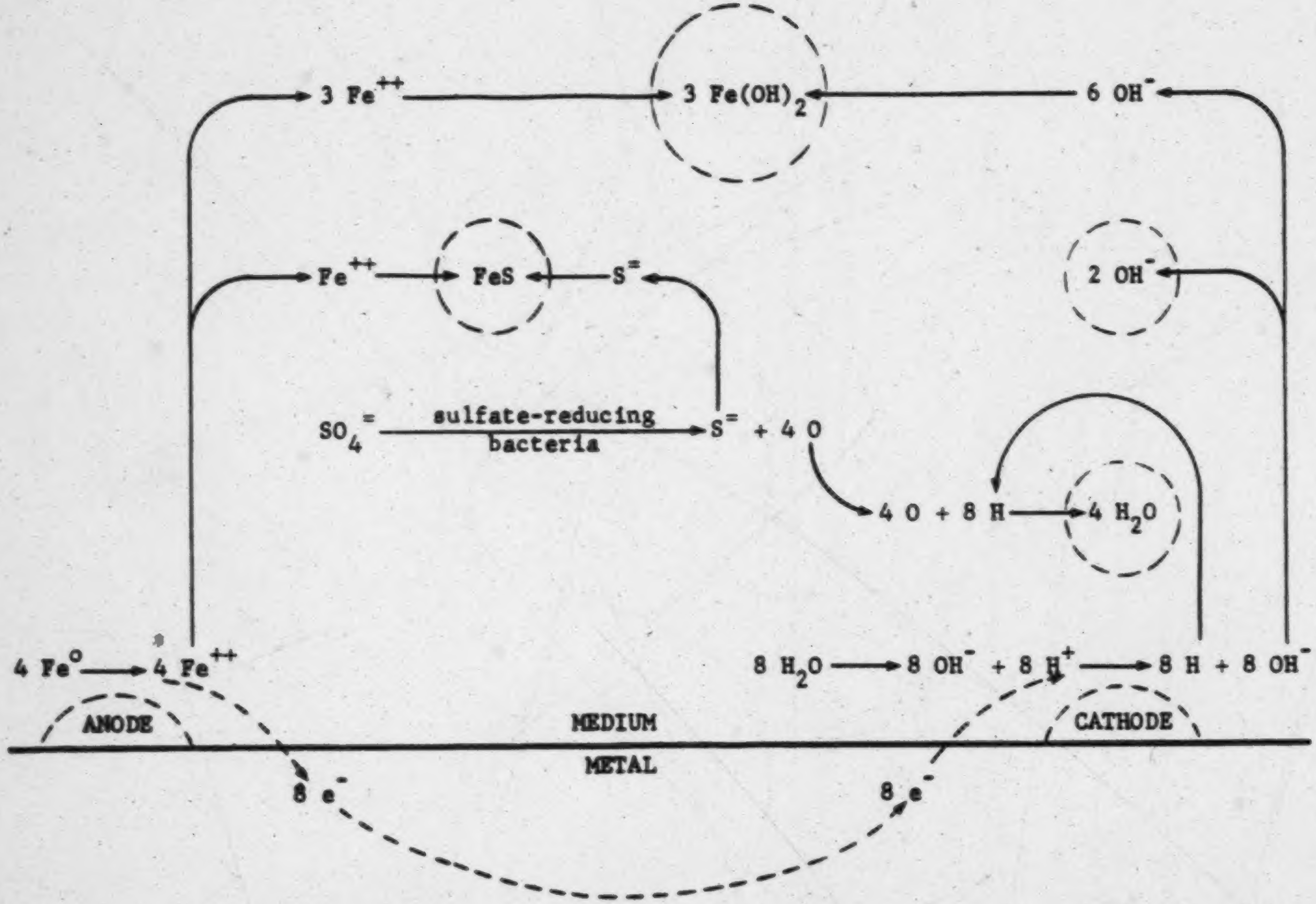

3 Fe++
3 Fe(OH)2
6 OH-
Fe++
FeS
S=
2 OH-
SO4=
sulfate-reducing
bacteria
S= + 4 O
4 O + 8 H
4 H2O
4 Fe°
4 Fe++
8 H2O
8 OH- + 8 H+
8 H + 8 OH-
ANODE
MEDIUM
METAL
CATHODE
8 e-
8 e-

Figure 6. Anaerobic corrosion of iron by the Theory of von Wolzogen Kuhr and Van der Vlugt.

effect of hydrogen sulfide (14). However, studies also have shown that corrosion by D. orientis is insignificant compared to that by D. desulfuricans, suggesting that the ability to bring about depolarization at the anode could not account for the entire effect of sulfate-reducing bacteria.

With regard to the promotion of anaerobic corrosion for the control of hydrogen sulfide in manure, there does not appear to be the need to know the exact mechanism of the corrosion process. However, if anodic depolarization via the reaction between Fe^{++} and H_2S is insufficient to induce corrosion, the rate of corrosion might be expected to be negligible in a sulfide-containing media which does not contain sulfate-reducing bacteria. In this regard, then, the question raised earlier concerning the relative importance of sulfate-reducing and putrefying bacteria as producers of hydrogen sulfide in manure may become especially pertinent.

(3) Chemical Oxidation:

When strong oxidizing agents are applied to manure, their primary effect is to oxidize all reduced inorganic compounds in the media. Oxidizing agents, added at less than the amount required for disinfection of the waste, should control hydrogen sulfide in manure by oxidizing the sulfide to elemental sulfur.

Faith (45) found that odors due to hydrogen sulfide in anaerobic sumps could be quickly eliminated by treatment with potassium permanganate. In agreement with what has been noted above, Faith postulated that potassium permanganate oxidizes odorous materials for rapid odor control and then, as a secondary effect, alters the bacterial population so that putrefying bacteria are not dominant.

(4) Biological Oxidation:

Biological oxidation as opposed to chemical oxidation may be an alternative means of reducing the concentration of hydrogen sulfide in manure storage facilities.

Many organisms are capable of oxidizing hydrogen sulfide to elemental sulfur or sulfate, but only three of the most important types will be mentioned here:

(a) Beggiatoa spp. oxidize sulfide to elemental sulfur and derive energy from the oxidation process (21). These bacteria require oxygen as the hydrogen acceptor and so are strict aerobes. The elemental sulfur formed during their energy metabolism is deposited as sulfur granules inside the cells. When the sulfide disappears, the granules disappear and sulfate is released to the media. However, Beggiatoa are not found commonly in waste storage ponds except in the very top layer where aerobic conditions exist (50).

(b) Thiobacillus denitrificans is an obligate anaerobe, utilizing nitrate instead of oxygen as a hydrogen acceptor for the oxidation of sulfide to sulfates (21). Butlin (20) proposed that anaerobic sulfide-containing media be innoculated with the organism to control hydrogen sulfide evolution.

(c) Photosynthetic sulfur bacteria represent two of the three families of photosynthetic bacteria (83):

(i) Thiorhodaceae - purple sulfur bacteria

(ii) Chlorobacteriaceae - green sulfur bacteria

(iii) Athiorhodaceae - non-sulfur purple bacteria.

The photosynthetic sulfur bacteria require light and strictly anaerobic conditions for growth. In such an environment, they utilize carbon dioxide as the hydrogen acceptor and hydrogen sulfide as the hydrogen donor in their energy yielding metabolism.

The prototype genus of the green sulfur bacteria is Chlorobium (21). These bacteria deposit sulfur outside the cell, are non-motile, and are usually unable to carry the oxidation of sulfur to sulfate. Their presence in waste stabilization ponds apparently has not been documented.

The best known genus of the purple sulfur bacteria is Chromatium (21). These organisms are motile, deposit sulfur internally and, like Beggiatoa, can oxidize the sulfur further to sulfate when the source of sulfide is diminished. Purple sulfur bacteria often grow so prolifically in waste lagoons that they impart a characteristic red or purple color to the sludge or water. Their presence in lagoons usually is accompanied by low odor levels.

Purple sulfur bacteria have been isolated from agricultural (119, 131) and domestic (50,64,83) waste lagoons. Meredith and Pohland (83) have shown that the growth and proliferation of these bacteria in waste stabilization ponds is dependent upon pH and temperature, the optima for Chromatium being 7.5 and 26.5^{o}C respectively. Iron was also found to be important and often limiting.

Photosynthetic sulfur bacteria appear to play an important role in waste stabilization ponds and effectively eliminate offensive odors due to hydrogen sulfide. Their innoculation into lagoons where they are not present naturally has been suggested as a practical means of odor control (119).

2.4.2 Minimize the Desorption of Dissolved Hydrogen Sulfide.

The second major alternative control of hydrogen sulfide associated with animal manure is to minimize the amount of dissolved hydrogen sulfide which is desorbed from solution. In Section 2.3.2, factors affecting the desorption of hydrogen sulfide from aqueous solution were outlined and included the solubility of the gas, the concentration of gaseous and dissolved hydrogen sulfide, and properties of the media including pH, temperature and surface conditions. The means by which control may be exerted over the pH and temperature of the media and the concentration of dissolved hydrogen sulfide, and the effects and practical limitations of such controls, were discussed in Section 2.4.1. Two controls not yet considered are dilution of the media and control over surface conditions.

2.4.2.1 Dilution.

If manure is diluted, the total capacity of the manure for dissolved gases is increased. At $0^{o}C$, the solubility of hydrogen sulfide in water is 437 $cm^3/100\ cm^3$ of water (27); clearly, if the volume of solvent is increased, the amount of gas which can be dissolved is increased porportionally.

Despite the fact that dilution does increase the amount of hydrogen sulfide gas which may be dissolved, dilution will not always reduce the amount of hydrogen sulfide gas released to the atmosphere. One group of researchers (76) reported that the odor from diluted manure is always more offensive than the odor from undiluted manure. Compared to undiluted chicken manure, the same manure when diluted evolves far greater amounts of hydrogen sulfide (77). Dilution causes a decrease in pH, resulting in greater amounts of dissolved hydrogen sulfide gas and also creates an environment which is more ammenable to sulfide production.

The two reports cited above are the only two reports which could be found in the literature concerning the effects of dilution on malodors from manure. The research upon which these reports were based compared diluted manure (fresh excreta diluted 3 to 1 by weight with distilled water) to undiluted fresh excreta. There is certainly reason to believe that if the diluted manure had been further diluted, the amount of hydrogen sulfide gas released would have been smaller. However, excessive dilution results in much larger quantities of material that must be stored and handled.

2.4.2.2 Surface Conditions.

Research cited in Section 2.1 of this review has shown that large quantities of hydrogen sulfide gas are released upon agitation of liquid manure. As long as the manure is left completely undisturbed, only small amounts of hydrogen sulfide are released. However, even a very slight disturbance of the manure surface can lead to dangerously high concentrations of hydrogen sulfide in the atmosphere above the manure. The act of agitation tremendously increases the effective area for desorption and hence increases the rate of desorption of dissolved hydrogen sulfide.

In an attempt to find some means of emptying manure pits without the characteristic large increase in hydrogen sulfide gas concentrations, research has been conducted in Germany (28) using 4 different methods. When the manure was removed with no agitation, the amounts of noxious gases were only slightly increased. Homogenization of the manure by hydraulic and mechanical means resulted in concentrations of hydrogen sulfide gas greatly exceeding the maximum recommended safe level of 2.0 ppm (volume basis), whereas lesser, but still high, levels of hydrogen sulfide were released upon pneumatic agitation. The authors suggested that some means, other than mechanical, hydraulic or pneumatic agitation, must be developed to allow the solids to be removed from manure pits without the danger of toxic gases. Further research clearly is needed on this subject.

2.4.3 Minimize the Dispersion of Gaseous Hydrogen Sulfide.

In addition to removing excess moisture and heat from livestock buildings, a third function of ventilation should be the removal of malodorous and toxic gases produced within the building. Not all ventilation systems presently being used perform the third function and fewer perform the function consistently well during all kinds of climatic conditions.

The installation of an adequate ventilation system, however, will not in itself constitute a satisfactory solution to all odor problems. In many cases, the problem merely is relocated from within the building to the area immediately surrounding the building. Although such odors associated with livestock facilities once were considered to be the "smell of money", they are now considered by neighboring residents to be obnoxious and often are the cause of court cases and hard feelings.

Some limited research has been directed toward the removal of malodors from ventilation before the air is exhausted. Most of the early attempts have been with filters of various types, as summarized in Table 5.

May et al. (82) suggested four alternative solutions to the problem of sulfur-containing malodorous compounds in air exhausted from poultry barns: (1) ultraviolet irradiation of the exhaust air to cause free radical formation and subsequent recombination and formation of less odorous compounds; (2) filter pads saturated with absorbent solutions to remove sulfur compounds; (3) wet scrubbing processes similar to those used for industrial processes; and (4) oxidation process such as exposure to open flame or catalytic oxidation. No results of research with these methods were given.

A search of the literature revealed that a large number of technically proven processes are available for the removal of hydrogen sulfide from gaseous emmissions. A summary of a few of these processes is given in Table 6. The major restraint to the widespread acceptance of these solutions to agricultural odor problems is clearly one of high cost.

2.5 Summary of the Literature.

The following observations and conclusions may be drawn on the basis of this review of the literature:

(1) Hydrogen sulfide produced during the anaerobic fermentation of livestock manure has been shown to be a major constituent of the

TABLE 5: SUMMARY OF RECORDED EXPERIENCE WITH FILTERS FOR REMOVAL OF HYDROGEN SULFIDE FROM VENTILATION EXHAUST AIR.

Type of Filter	Mechanism of odor removal	Comments
Soil filters (54)	biological stabilization ion exchange water solution adsorption contact catalysis	Hydrogen sulfide removal efficiencies were much greater with biologically active soil than with sterile soil, and, in the case of sterile soils, were much greater with soil in the dry rather than the wet condition. Factors affecting the design of an effective soil filter were outlined.
Plastic foam-pad filter (40)	mechanical removal on dust particles	Rapid clogging of the filters combined with ineffective cleaning methods and high initial cost were deemed to make this method impractical.
Baffle impringement filters with a water spray ahead of the baffles (130)	water solution adsorption mechanical removal on dust particles	Odors were substantially but not completely removed. The system would require modifications for cold weather operation.
Biological filter (110)	biological stabilization water solution mechanical removal on dust particles	The filter is constructed of phenol-coated honeycomb paper with provision for water washing. Initial results are promising and research is continuing.
Activated Carbon filter (62,91)	chemisorption (catalytic oxidation at adsorption site)	Activated carbon filters are very effective for hydrogen sulfide removal at low air flow rates and low concentrations of hydrogen sulfide, but are very expensive to construct and operate.

TABLE 6: EXAMPLES OF PROCESSES EMPLOYED FOR REMOVAL OF HYDROGEN SULFIDE FROM GASEOUS INDUSTRIAL EMISSIONS.

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1. Hydrogen sulfide is removed selectively from exhaust gases by absorption of the gas into solutions of strong oxidizing agents such as potassium permanganate, sodium dichromate or ferric salts, or into a bed of hydrated ferric oxide. Hydrogen sulfide also may be absorbed selectively into solutions of ammonium thio-arsenate or potassium dimethylglycine, or into an aqueous suspension of iron hydroxide. Hydrogen sulfide absorbed by any of these methods can be recovered by oxidation to sulfur under the catalytic influence of iron or nickel salts; however, these processes are all very expensive, even when the sulfur is recovered. A more economical method for selective removal of hydrogen sulfide involves absorption of the gas into a strong carbonate-bicarbonate solution (96).

---

2. Air containing hydrogen sulfide is passed through an electrode where glow discharge is carried out with a current of 0.264 amps at 825 volts and 218 mm pressure. Elemental sulfur with a purity of 99.6% is recovered from the process (81).

---

3. Fumes containing small amounts of hydrogen sulfide are purified efficiently by treating at 100 - 150^{0} C with activated Al_2O_3 with subsequent regeneration of the aluminum oxide catalyst (113).

---

4. By the Clause process, hydrogen sulfide is converted to elemental sulfur in a two-stage reaction. First the gases containing hydrogen sulfide are mixed with oxygen in a furnace over bauxite catalyst to yield sulfur dioxide. Then the sulfur dioxide produced is reacted with more gases containing hydrogen sulfide in another furnace with recovery of elemental sulfur. The sulfur recovered is reputed to pay for the process when the gases used contain 7 - 10% hydrogen sulfide (46).

---

5. As in 4 above, except that the process is carried out in an activated carbon bed maintained at high temperatures (16).

---

6. The gaseous emissions from a sewage treatment plant are scrubbed with sewage effluent which removes hydrogen sulfide by dissolution (98).

---

characteristic manure odor and is known to adversely affect the health of livestock and farm operators. Control of this and other volatile sulfur-containing compounds is essential to the continuation of the current regard for liquid manure systems as a feasible waste management alternative.

(2) Sulfur-containing gases are produced by way of biological and bio-chemical transformations from sulfur compounds in manure. However, little is known with respect to the total sulfur content of manure, the forms in which sulfur occurs in manure, and transformations of sulfur during prolonged storage of manure. Such information on the sulfur status of manure is basic to an understanding of possible odor control methods involving the control of hydrogen sulfide and other volatile sulfur compounds.

(3) Whereas control may be exercised over the desorption of dissolved hydrogen sulfide from the manure solution or the subsequent dispersion of gaseous hydrogen sulfide throughout the surrounding atmosphere, perhaps a more "grass-roots" approach may be taken in which large concentrations of hydrogen sulfide are not permitted to accumulate in the manure. In particular, chemical control of hydrogen sulfide would appear to offer several advantages including lower capital costs and convenient adaptability to existing waste management facilities. Potentially effective chemicals include metals for precipitation of sulfides, lime or other alkaline compounds for pH elevation, and oxidizing agents for selective ORP control and oxidation of dissolved hydrogen sulfide.

(4) From the standpoint of acquisition and safety in handling, iron

appears to be the most suitable metal for precipitating sulfides from manure. Ionic iron has been used successfully to precipitate sulfides from anaerobic digestors receiving domestic sewage sludge, but its effectiveness in manure solutions apparently has not been demonstrated. Sulfides also may be precipitated by iron ions released to solution by the corrosion of metallic iron. The rates of corrosion, and consequently the effectiveness with which soluble sulfides are removed from solution, that might be expected upon addition of metallic iron to anaerobic manure are unknown.

(5) Some limited experience with lime for odor control from manure has been recorded. Lime perhaps may exert an effect on odors released from anaerobic manure by retarding bacterial action or by minimizing the volatilization of soluble odorous constituents. Information is needed to determine more clearly the specific effect of liming on hydrogen sulfide produced in, and released from, anaerobic manure.

(6) Chemical oxidizing agents may offer an alternative to aeration as a means of controlling the oxidation-reduction potential of stored animal manure. Strong oxidizing agents also might be expected to remove reduced sulfur compounds from the manure solution by oxidizing them to elemental sulfur. Added in excess, these oxidizing agents may further exert an effect on odor production by destroying the bacteria which cause odors. Research is required to evaluate the effectiveness of some common oxidizing agents for controlling hydrogen sulfide production from anaerobic manure.

3. OBJECTIVES

The following objectives were considered in this research project:

(1) to investigate the amounts and forms of sulfur in the feces and urine of feeder pigs.

(2) to investigate the amounts and forms of sulfur in samples of liquid swine manure and other wastewaters collected from commercial swine operations.

(3) to determine the effects of aerobic and anaerobic storage of liquid swine manure on the sulfur status and the nitrogen: sulfur ratio of the manure.

(4) to determine the effect of several oxidizing agents, lime and various forms of iron on:
   (a) the amount of hydrogen sulfide gas evolved from anaerobically-incubated swine manure,
   (b) the amount of hydrogen sulfide gas released upon agitation of anaerobically-incubated swine manure, and
   (c) the total amount of hydrogen sulfide produced in anaerobically-incubated swine manure.

(5) to elucidate the mechanisms whereby each of the above-mentioned chemicals exert their specific effects on hydrogen sulfide production in and/or release from anaerobic manure.

(6) to evaluate the potential practical applications of each of the above-mentioned chemicals.

4. EXPERIMENTAL PROCEDURE

4.1 Materials.

4.1.1 Laboratory Digestors.

Most of the laboratory trials in this study were conducted using six conical-shaped glass vessels (Figure 10). The vessels, hereafter termed laboratory digestors, were made from 2800 ml pyrex Fernbach-Type flasks by personnel of the Scientific Glassblowing Services, Chemistry Department, University of Alberta. A short piece of 1/2 in. tygon tubing was affixed to the funnel-shaped bottom of each flask and secured with a hose clamp. The digestors were closed by clamping the tubing with a screw clamp. The neck of each flask was fitted with a No. 13 rubber stopper (Figure 7).

To accomodate the necessary gas sampling ports, three holes were burned into each stopper. The centre hole accepted a 1/4 in. sintered-glass diffusion tube. The diffusion tube could be adjusted to either just sweep the surface of the digestor contents with a carrier gas or to bubble gas from the bottom of the digestor. The other two holes in each stopper accepted 1/8 in. glass tubes which could be used as gas outlets or as ports for the addition of chemicals.

A second set of six laboratory digestors were used in one trial near the end of the experimental period (Figure 11). These digestors were constructed from 1-gallon nalgene sample bottles with plastic screw caps. The containers were sealed by wrapping the threads of the bottle with teflon tape. Holes were punched into the centres of the hard plastic caps to accommodate 2-hole No. 6 rubber stoppers. Each stopper was fitted with a 1/4 in. sintered glass gas diffusion tube, the tip of which extended to the bottom of the digestor, and a 1/8 in.

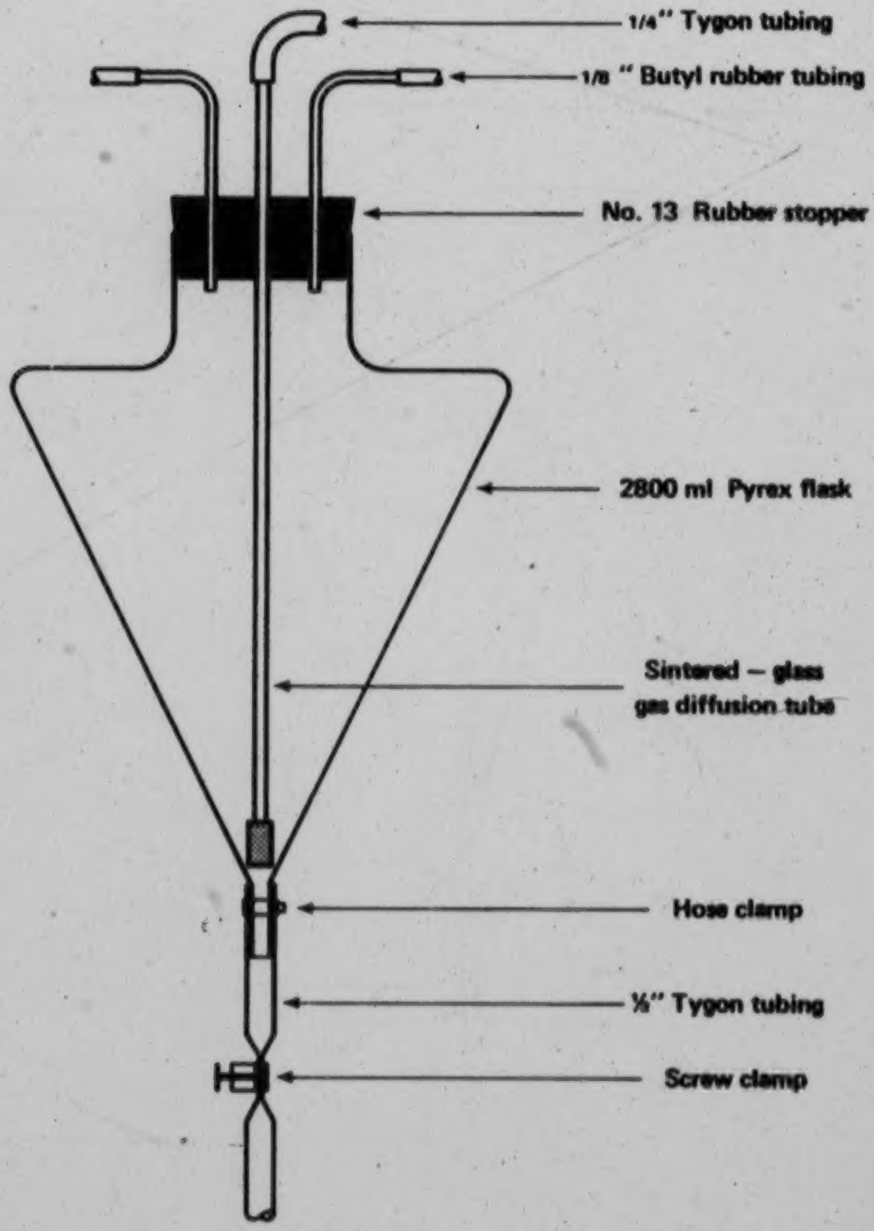
1/4" Tygon tubing
1/8 " Butyl rubber tubing
No. 13 Rubber stopper
2800 ml Pyrex flask
Sintered – glass gas diffusion tube
Hose clamp
½" Tygon tubing
Screw clamp

Figure 7. Schematic of glass laboratory digestor.

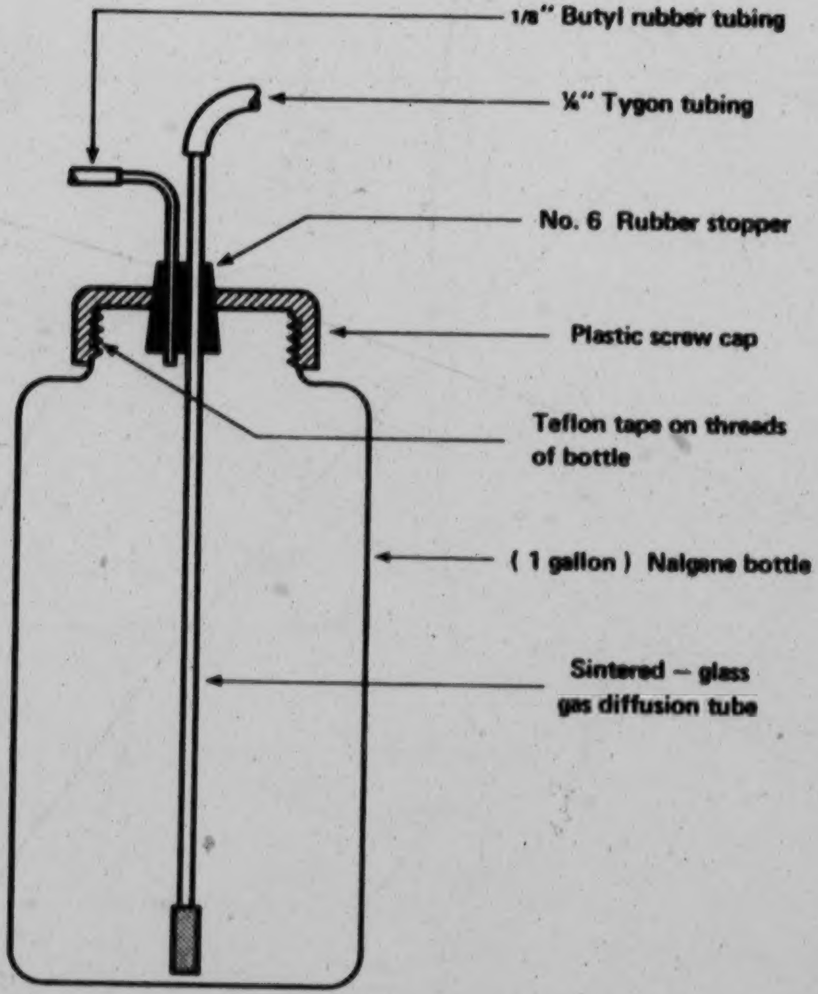
1/8" Butyl rubber tubing
¼" Tygon tubing
No. 6 Rubber stopper
Plastic screw cap
Teflon tape on threads of bottle
(1 gallon) Nalgene bottle
Sintered – glass gas diffusion tube

Figure 8. Schematic of plastic laboratory digestor.

glass tube as a gas outlet (Figure 8).

The glass digestors were chosen initially over the plastic digestors for the following reasons:

(1) The transparency of the glass digestors enables a visual inspection of the digestor contents.

(2) Plastic containers are not reliable for repeated tests requiring odor evaluation (5).

(3) Glass containers may be modified more easily with respect to shape and associated fixtures than plastic containers. The conical shape of the glass digestors also facilitates mixing of the digestor contents.

(4) Plastics adsorb phosphorus and certain other materials more readily than glass, and may permit ammonia to escape (5).

4.1.2 Bench-scale Digestors.

Three bench-scale digestors were constructed in the Agricultural Engineering Workshop, University of Alberta, from used 46-gallon metal drums (Figure 12). After removing the original tops and thoroughly cleaning the drums, a 1/8 in. iron plate with a 12 in. diameter opening in the centre was welded onto the top of each drum. The large opening was necessary to facilitate filling and emptying of the digestors, and to better simulate an open storage tank. A removable 1/2 in. iron cover-plate was fitted over the opening and fastened with 6 1/2 in. steel bolts. A rubber gasket and a thin coating of silicone grease were required to secure a gas-tight seal between the cover plate and the drum top. Since manure is known to be corrosive to metal, the drums were sprayed on the inside with several coats of liquid plastic which formed a thick protective coating (Figure 9).

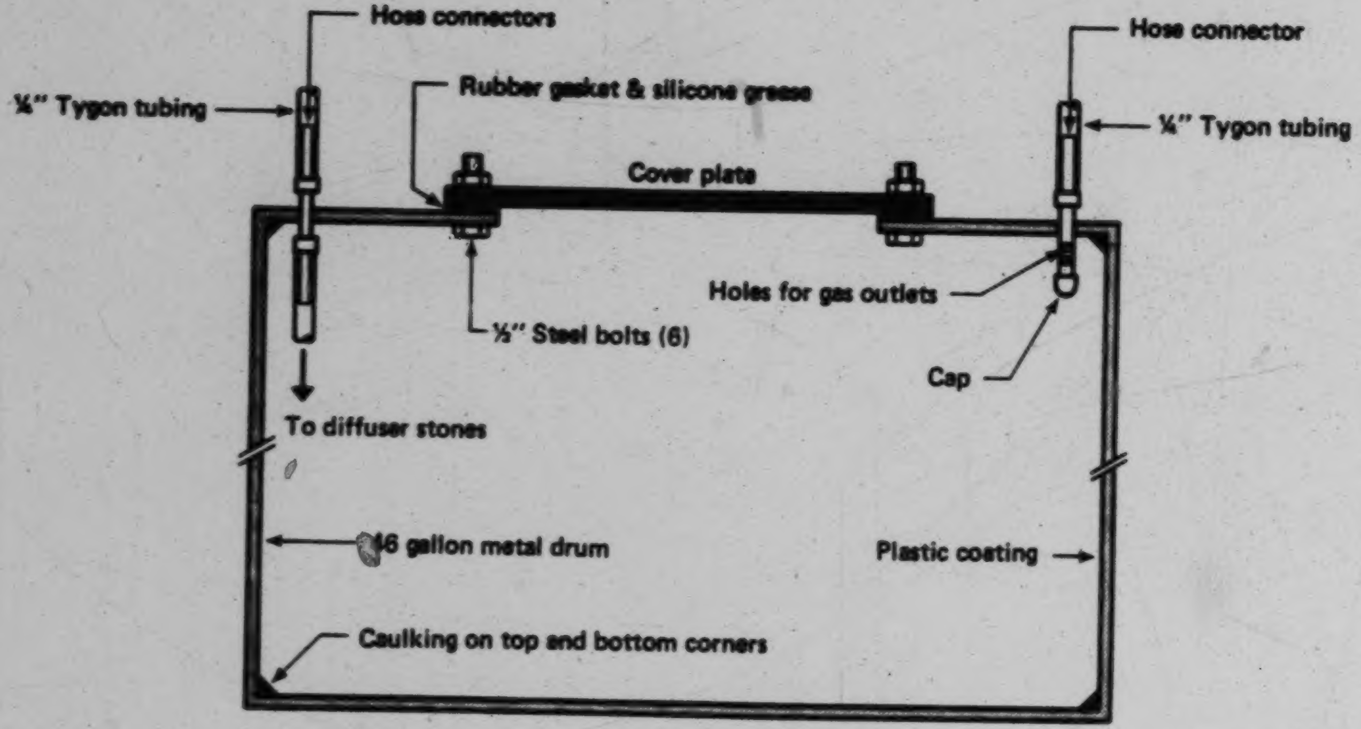
Hose connectors
¼" Tygon tubing
Rubber gasket & silicone grease
Cover plate
Hose connector
¼" Tygon tubing
Holes for gas outlets
½" Steel bolts (6)
Cap
To diffuser stones
16 gallon metal drum
Plastic coating
Caulking on top and bottom corners

Figure 9. Schematic of bench-scale digestor.

Figure 10. Glass laboratory digestors in operation.

Figure 11. Plastic laboratory digestors in operation.

Figure 12. Bench-scale digestors in operation.

Figure 13. Gas-diffuser apparatus used in bench-scale digestors.

The cover plate was tapped at either edge of the drum on one diameter. Short steel nipples were brazed into the holes. On one nipple, a hose connector was screwed onto the outer end while the inner end was capped. Immediately inside the cap, two small holes were drilled into the nipple to allow gases to escape but to prevent the digestor contents from splashing out. The other nipple was fitted on both ends with hose connectors. Extending from the interior nipple, a series arrangement of five gas-diffusion stones was suspended vertically in the digestor and kept in place by a supporting thin steel plate (Figure 13).

To facilitate handling of the drums when full, a barrel frame was constructed from square tubular steel and scrap iron plates. The drums could be tipped over or moved from place to place easily with the aid of the frame.

4.2 Sources of Manure Samples.

4.2.1 Installation A.

This pig production unit is a totally confined farrow-to-finish operation with a one-time capacity of 90 sows, 180 weaner pigs and 500 - 600 feeder and finisher pigs. Manure from the dry-sow stalls, breeding pens, farrowing crates and weaner-pig crates is scraped daily into shallow gutters and flushed into a pit beneath the feeder and finisher barn. The finisher barn is 115 feet x 24 feet and accommodates two rows of pens along the long axis of the building. Two manure pits, each 4 feet wide by 32 inches deep run the length of the building beneath the slatted portion of the partially slatted floor. Every 4 to 5 days, a plug is pulled at the end of each pit, allowing the contents to empty by gravity into either one of two primary cells in a

3-cell lagoon system.

About 2150 gallons/day of water are used at the installation for cleaning and drinking purposes. The rations fed consist largely of ground barley and wheat, and soybean meal supplements. A full description of the rations received by the weaner pigs, sows and feeder pigs is given in Appendix B.

Odor and dust levels in the finisher barn are quite high. After remaining in the barn for 30 to 40 minutes to collect samples, the author experienced throat and nose irritations, presumably due to the high ammonia and dust concentrations. Since the owners had experienced difficulty in emptying the anaerobic primary cells of the lagoon system in the spring, the pits beneath the floor could not be emptied completely. This caused a build-up of anaerobic manure in the bottom of the pits. During one short portion of the collection period, the owners experimented with commercial enzyme preparations for odor control. They claimed only moderate success with the enzymes and discontinued their use.

4.2.2 Installation B.

The production unit in this case consists of a 1000 - head capacity, partially slatted-floored finishing barn, a farrowing barn and several small, non-insulated sow pens. Manure from the pens is allowed to drain down a concrete channel into an anaerobic lagoon. Manure from the finisher barn is collected in pits beneath the floor and drained by gravity flow into two other anaerobic lagoons. An underground holding tank is used to collect the manure and wastewater from the farrowing barn. This tank is emptied completely every 10 days by a manure tanker-wagon.

Of the three anerobic lagoons being used, the two receiving manure from the finisher barn were dark in color with accumulations of sludge extending above the liquid level in several places in early summer. In contrast, the lagoon receiving wastes from the sow pens has a distinct red color on the surface and had a less offensive odor than the other lagoons. The red-colored layer was underlain by a black, foul-smelling sludge. The red color and lack of offensive odor probably could be due to the presence of photosynthetic sulfur bacteria.

In an attempt to control odors in and around the farrowing barn, a commercial odor-control product was being used. The mode of action of the product is not known but is thought to involve an alteration of the bacterial population to include a dominance of non-putrefying bacteria. Manure which was being treated with the chemical was very dilute and had a slight chemical odor that was considered by the owners to be less offensive than the usual manure odor.

4.2.3 Installation C.

This operation involves two feeder barns with a combined capacity of 500 head. All manure and wastewater is collected in deep narrow gutters and flushed into an underground holding pit (12 feet x 18 feet x 8 feet). This pit is emptied every ten days by an 1100 - gallon truck-mounted vacuum manure-tanker, the liquid manure being spread on surrounding farm land. The ration fed to pigs at this installation consisted of ground barley and a commercial swine grower-supplement (Appendix B).

Odor levels at and near the holding tank were quite high under normal operating conditions and were intensified during pumping-out of the manure. However, the odor was that of fresh manure and has not drawn any complaints from nearby residents to date.

4.2.4 Installation D.

This installation is one of the research facilities located at the Edmonton Research Station, University of Alberta. Swine in this instance are used in various feeding and metabolism trials by researchers of the Department of Animal Science, University of Alberta.

4.3 Manure Sampling Methods.

4.3.1 Installation A.

Initially, an attempt was made to collect samples of manure from the underfloor manure pits by stirring the pit contents and dipping with a long-handled dipper. However, complete homogenization of the pit contents, even in a localized zone, was difficult to attain and the samples collected appeared to contain proportionally less solids than were present in the actual body of stratified manure. Furthermore, the voluntary creation of turbulence was considered to be somewhat questionable since dissolved gases are liberated in the process, thereby changing the chemical characteristics of the waste.

Accordingly,two manure samplers were designed and constructed for collection of representative samples of slurry from the manure pits without the need for agitation. These two samplers and the long-handled dipper previously mentioned are shown in Figure 14. Both samplers were designed to collect vertical profiles of material from the body of manure which, in its unmixed state, contained stratified layers of liquids and sludge. The ability of these samplers to perform this function was evaluated by comparing the solids content of samples collected by each to the solids content of a sample collected by mixing and dipping.

One of the samplers, termed a core-slider sampler, was constructed of lightweight aluminum plates riveted together and sealed with an epoxy glue (Figure 15). A teflon slide moves within a curved grooved guide at the bottom of the sampler (Figure 16) and is activated by a control-arm at the top. To collect a sample, the sampler was lowered slowly into the manure in the vertical plane, with care taken to create as little disturbance as possible. The slide was kept open by exerting pressure on the control-arm until the sampler was lowered to the bottom of the pit. The slide then was closed by pulling on the control-arm and the sampler raised to the surface.

The other sampler, termed a core-plug sampler, was patterned after a point-sampler designed by Aasen (1). This sampler was constructed of a 2-inch aluminum pipe which slides over a 1/4 inch iron rod attached to a teflon plug at either end (Figure 15). The sampler was used in a two-step operation. Firstly, the rod with the streamlined plug was lowered into the manure pit and rested on the bottom. After a certain length of time (at least 15 minutes) required for the pit contents to re-establish equilibrium around the rod, the tube was lowered carefully down over the rod and seated on the plug at the bottom. Another plug then was introduced on the top and the entire sampler tightened together with a large wing nut.

Samples collected with each of these integrated-depth samplers were found to contain much greater amounts of settleable solids (up to 100% more) than dipped samples of the mixed slurry and, on this basis, were considered to be more representative of the larger body of manure. The core-slider sampler was chosen for all further sampling

Figure 14. The three types of manure samplers tested.

Figure 15. Major components of the integrated-depth manure samplers.

Figure 16. Close-up view of the sampling tip of the core-slider manure sampler.

at Installation A since apparently identical samples were collected by each, yet the core-slider sampler was more convenient to use.

4.3.2 Installation B.

Manure from the holding tank, which had been treated with the odor control chemical, was sampled directly from the tanker-wagon as the wagon was being emptied. A portion of the sample was collected from each of two or three loads to ensure that a representative sample was obtained.

The red-colored lagoon receiving manure from the sow pens was sampled with a dipper on the end of a 20-foot lightweight metal pipe. Only the top foot of material was sampled. The manure pits in the finishing barn, and the lagoons into which they emptied, were not sampled during this investigation.

4.3.3 Installation C.

Samples of manure from the holding tank were collected from the vacuum-tanker during the field spreading operation. As the tanker moved along the field, samples were collected by holding a sample bottle in the stream of manure being forced out of the tanker. Shoulder-length plastic veterinarian gloves were worn to make the job less offensive. The general procedure was to take part of the sample from each of two or three loads to secure a sample which might be considered representative of the holding-tank contents.

4.3.4 Installation D.

Samples of manure obtained from Installation D were collected in conjunction with a metabolism trial involving rapeseed diets fed to feeder pigs. Feces and urine were collected separately by holding individual pigs in specially-designed metabolism crates. Excrement was collected from eight pigs for three days in each of four collection periods. Each day's collections from each animal were stored at 4°C until the end of the 3-day collection period when the individual samples were bulked to form a composite sample. Subsamples for this investigation were collected in 250 - ml plastic bottles from the composite samples, and frozen prior to chemical analyses.

4.4 Preparation and Storage of Manure Samples.

All samples of manure collected from Installations A, B and C were brought into the Agricultural Engineering Laboratory, as soon as possible after collection, in 1-gallon nalgene bottles. Except for manure which was to be used in incubation trials, each entire sample was blended at 10,000 rpm with a Waring blender. The only analyses performed on the unblended samples were a visual inspection of color and pH determinations.

Foaming was a major problem encountered during the blending process. Blending was observed to cause an increase in sample pH of 0.3 to 0.5 pH units, probably due to the loss of carbon dioxide. In all likelihood, blending also resulted in the loss of other volatile manure constituents including ammonia and hydrogen sulfide. However, the blending process was considered necessary to obtain a homogeneous sample from which representative subsamples could be withdrawn.

After blending, the samples were allowed to remain quiescent for thirty minutes in closed containers to reduce the amount of entrapped air. Two representative subsamples of about 100 grams each then were withdrawn from each sample for total solids determinations.

Because of the limited availability of laboratory expertise and facilities, chemical analysis of the samples could not be performed on each sample as collected, thereby necessitating storage of the samples. Five 250 ml subsamples were withdrawn from each blended sample into screw-cap plastic bottles, these being frozen immediately in a deep-freeze unit. In the frozen condition, the nitrogen and sulfur balances would be expected to remain unaltered even after extended periods of storage (2). Several small subsamples, rather than a single larger one, were collected from each sample to allow individual analyses to be performed on the sample at different times without having to thaw out the entire sample each time. The collection and storage of five subsamples guaranteed sufficient material for duplicate and check analyses where desired.

4.5 Investigations Into the Sulfur Status of Fresh Swine Excreta.

Samples of fresh urine and feces were supplied by researchers from the Department of Animal Science. Thirty urine samples and the same number of feces samples had been collected during a feeding trial involving six rapeseed diets and two diets containing no rapeseed fed to four groups of feeder pigs. The diets fed are described in Appendix L.

Although the initial intent of this investigation into the sulfur status of fresh swine excreta was simply to obtain data on the amounts and forms of sulfur in a few samples of urine and feces, the nature of the animal science feeding trial presented an opportunity to investigate the effects of different diets on sulfur excretion. For purposes of this investigation, therefore, equal-sized portions of the three-day collection of feces and urine from each of the six animals receiving rapeseed diets were bulked to form a single composite sample of feces and urine. Similarly, the excreta from the two animals not receiving rapeseed in their diets were bulked. Since four separate collection periods (i.e., four different groups of pigs) had been involved in the feeding trial, four samples of each of feces and urine were ultimately collected for each of the two treatments. These samples were analyzed for total sulfur and total sulfate-sulfur in the laboratories of the Department of Soil Science, University of Alberta.

In order to relate sulfur excretion to sulfur intake, the feed records kept by the cooperating animal scientists were obtained, as were samples of the feed for sulfur analysis. Data on the nitrogen content of the feed, total feed intake by each animal, total fecal and urinary excretion by each animal, and the nitrogen content of both the feces and urine also had been collected and were made available to the author. These data are given in Appendix G. Mean values were calculated from the data to correspond to the grouping that had been carried out for the sulfur analyses. These mean values are reported, together with the sulfur data, in Appendix H.

4.6 Investigations Into the Sulfur Status of Swine Manure and Wastewaters.

All manure and wastewater samples collected from Installations A,B and C were analyzed for total nitrogen, total sulfur and total sulfate-sulfur. Selected samples were subjected to either aerobic or anaerobic storage for periods of approximately three weeks at room temperature (70°F) and analyzed again for the same three constituents.

All analyses for nitrogen and sulfate-sulfur were performed at the Soil and Feed Testing Laboratory, O.S. Longman Building, Edmonton, according to their standard procedures (3) used for soil and feed samples. All samples were analyzed for total sulfur in the Department of Soil Science Laboratories and in the Soil and Feed Testing Laboratory.

4.6.1 Aerobic Storage.

Two liquid manure samples were subjected to aerobic storage under controlled laboratory conditions. The procedure followed in each of these two aerobic incubation trials was identical and is outlined below:

(1) 2000 grams of manure were weighed into a glass laboratory digestor.

(2) The inlet gas diffusion tube was positioned to bubble gas from the apex of the cone. Air was supplied into the digestor at an unmetered level sufficient to keep the digestor contents mixed while, at the same time, supposedly maintaining completely aerobic conditions.

(3) At the end of the incubation period (approximately three weeks), the digestor contents were analyzed for pH and then blended at 10,000 rpm with the Waring Blender. Duplicate 100-gram subsamples were removed for total solids determinations and five 250-ml subsamples were frozen prior to chemical analyses.

4.6.2 Anaerobic Storage.

Four liquid manure samples were subjected to anaerobic storage under controlled laboratory conditions. The procedure followed for each of these anaerobic incubation trials was as follows:

(1) Approximately 3500 grams of manure were incubated in a closed 1 gallon nalgene container.

(2) During the incubation period, the containers were left completely undisturbed.

(3) At the end of the incubation period (approximately four weeks), the digestor contents were handled in a manner identical to that described for the aerobically-incubated material.

4.7 Chemical Control of Hydrogen Sulfide from Anaerobic Manure.

4.7.1 General Description of Laboratory Incubation Trials.

On the basis of an extensive literature search, seven potentially effective chemicals were selected for further investigations. These chemicals are listed in Table 7 together with the chemical formula and most probable mode(s) of action of each.

TABLE 7: CHEMICALS SELECTED FOR LABORATORY INVESTIGATIONS.

Name	Chemical Formula	Principle Mode of Action
Iron:		
Metallic iron	Fe^{0}	Precipitates sulfides as iron sulfide (e.g., FeS, Fe_2S_3)
Ferrous iron	Fe^{++}	
Ferric iron	Fe^{+++}	
Nitrate	NO_3^-	Weak oxidizing agent
Ammonium persulfate	$(NH_4)_2S_2O_8$	Strong oxidizing agent
Potassium permanganate	$KMnO_4$	Strong oxidizing agent
Lime(calcium hydroxide)	$Ca(OH)_2$	Elevates the pH of the media

These chemicals were evaluated for their effect on the amount of hydrogen sulfide gas released from anaerobically-stored swine manure by incubating multiple subsamples of a particular manure sample, treating all but one of the subsamples with the various chemicals, and comparing the hydrogen sulfide released from each to that released by the untreated subsample. Since the literature search was continuing at the same time that the trials were being conducted, and since the investigations reported were to be of an exploratory nature, no attempt was made to incorporate a rigid statistical design into the experimental layout. Each chemical was used in at least two trials, but with a subsample of a different raw manure sample each time. An outline of the chemical treatments applied during each trial is provided in Table 8. The trials were conducted during four consecutive periods, each of approximately four weeks duration.

The same general procedure was followed in each of the trials, and each digestor involved in a particular trial was treated identically. At the beginning of each trial, 2000 grams of raw manure were weighed into each of six glass laboratory digestors except in trials II and IV when 1 and 2 digestors, respectively, were used for other investigations. After filling the digestors with manure, the inlet gas-diffusion tubes were adjusted to sweep gas across the surface of the manure. This was expected to simulate, as closely as possible, actual storage conditions in the field. Furthermore, by continually flushing manure gases out of the digestor, the rate of production of these gases by the fermenting manure could be monitored.

After approximately four days of incubation, the chemical treatments were applied and the incubation continued for another 16

TABLE 8: DESCRIPTION OF LABORATORY INCUBATION TRIALS

Trial	Manure Used	Treatment	Description
I	A-0811 (2000 gm)	Control	-
		Ferrous + Metallic iron	$FeCl_2.4H_2O$ - 1.2 gm Powdered iron - 20 gm
		Ferric iron	$FePO_4$ - 28.4 gm
		Metallic iron	Powdered iron - 20 gm
		Lime	$Ca(OH)_2$ - 30 gm
		Nitrate	$NaNO_3$ - 10.6 gm
II	C-0907 (2000 gm)	Control	-
		Ferrous + Metallic iron	$FeCl_2.4H_2O$ - 0.6 gm Iron rod - 20 gm
		Metallic iron	Powdered iron - 20 gm
		Lime	$Ca(OH)_2$ - 20 gm
III	C-1015 (2000 gm)	Control	-
		Ferric iron	$Fe_2(SO_4)_3$ - 5.3 gm
		Metallic iron	Iron rod - 20 gm
		Nitrate	$NaNO_3$ - 19.8 gm
		Ammonium persulfate	$(NH_4)_2S_2O_8$ - 20 gm
		Potassium permanganate	$KMnO_4$ - 100 ml Concentrated solution (2 gm)
IV	A-1108 (2000 gm)	Control	-
		Metallic iron	Iron rod - 20 gm
		Ammonium persulfate	$(NH_4)_2S_2O_8$ - 20 gm
		Potassium permanganate	$KMnO_4$ - 5 gm

to 21 days. During the entire incubation period, hydrogen sulfide gas released by the manure in each digestor was monitored continuously. The carbon dioxide produced in each digestor was monitored every two to four days for approximately three to six hours. At the end of the incubation period, the amount of hydrogen sulfide gas released by agitation of the digestor contents, and the total sulfide content of the digested material, were measured.

4.7.2 Gas Sampling and Analysis.

A schematic of the gas-sampling apparatus used in these trials is shown in Figure 17. The nitrogen carrier-gas was supplied from a pressurized cylinder. The gas, as purchased, contained small amounts of carbon dioxide which were removed during the carbon-dioxide monitoring period by passing the gas through a Fisher-Milligan gas-scrubber (Figure 18) containing barium hydroxide. The carrier-gas entered the digestors through sintered-glass gas diffusion tubes and was allowed to escape continuously through ports in the digestor tops. The gas leaving each digestor, carrying gases released by the manure, was conducted through a two-stage gas-scrubbing train consisting of two conventional gas-scrubbers connected in series (Figure 19).

The gas-scrubbers were large test tubes (28 mm x 200 mm) fitted with 2-hole No. 6 rubber stoppers. The gas inlet tube in each scrubber was a 1/8 in. glass tube extending to within 1/4 in. of the bottom of the tube. The orifice at the end of the outlet was reduced to 1/32 in. to produce smaller bubbles. The tubes were filled to a depth of 5 1/2 in. with an appropriate absorbent solution. Tygon tubing was used to connect the source of the carrier-gas to the digestor inlets, while butyl rubber tubing was chosen for all other

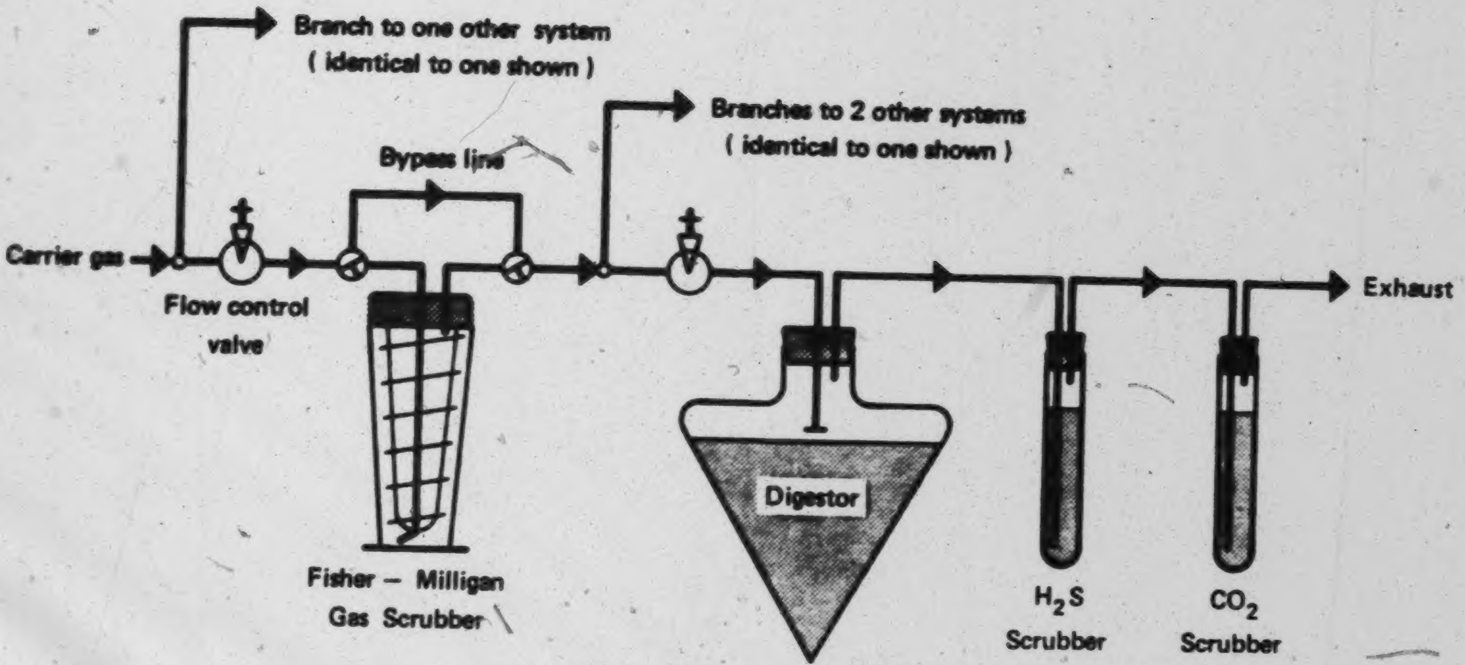
Branch to one other system
(identical to one shown)
Branches to 2 other systems
(identical to one shown)
Bypass line
Carrier gas
Flow control valve
Exhaust
Digestor
Fisher – Milligan Gas Scrubber
H_2S Scrubber
CO_2 Scrubber

Figure 17. Schematic of equipment used in laboratory incubation trials to monitor gases from fermenting manure.

Figure 18. View of Fisher Milligan gas-scrubbers.

Figure 19. View of conventional gas-scrubbers.

connections involving the gas scrubbers because of its greater pliability.

The first gas-scrubber in the absorption train contained a solution of cadmium acetate[a] in which hydrogen sulfide is trapped as insoluble cadmium sulfide (Ksp = 4×10^{-29}). Only one scrubber was used to trap the hydrogen sulfide from each digestor as preliminary trials had shown hydrogen sulfide recoveries in a single scrubber to be close to 100 percent. Every two to five days, the scrubbers were changed and the amount of hydrogen sulfide released during the collection period was calculated from the weight of dry cadmium sulfide precipitate collected during that period[b].

The second scrubber in the absorption train contained barium hydroxide solution[c] in which carbon dioxide is trapped as insoluble barium carbonate (Ksp = 8×10^{-9}). Initial attempts to use a single scrubber for collection of carbon dioxide indicated recoveries of less than 90 percent. Addition of a few drops of n-butanol to each scrubber, however, boosted the efficiency of a single scrubber to nearly 100%. Because of the problems associated with handling the copious amounts of carbon dioxide released from manure, the rate of carbon dioxide generation was monitored only for a few hours every two to four days. The rate of production of carbon dioxide over the sampling period, which was assumed to be representative of the rate of production over the longer incubation period, was calculated from the weight of dry barium carbonate collected[c] during the sampling period.

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[a] See Appendix D for formula for cadium acetate solution.
[b] See Appendix E for sample calculation.
[c] See Appendix D for formula of barium hydroxide solution.

4.7.3 Chemical Treatments.

During the first four days after the beginning of the incubation period, the amounts of hydrogen sulfide and carbon dioxide released from each digestor were monitored to ensure that all digestors were behaving similarly. On the fourth day, the chemical treatments were applied. Whereas the initial intent was to add chemicals through small ports in the top of the digestors, the procedure finally adopted involved removing the entire top just long enough for the chemicals to be added and stirred into the manure. Since the weight of chemical added was not the same in every case, sufficient distilled water was added to make a total addition of 100 grams to each digestor, including the control.

The quantities of chemicals added in each treatment are given in Table 8. The weight of chemical added in the initial trial with each treatment was based largely on recommendations from the literature and rough calculations from theory, tempered by experience and practical limitations. Subsequent estimates for a second trial with the same treatment were based largely on the experience gained from previous trials. A summary of the calculations and logic involved in estimating the quantities of chemicals required is outlined in Appendix F.

4.7.4 Hydrogen Sulfide Released by Agitation.

Sixteen to twenty days after the application of the chemical treatments, the contents of each digestor were agitated and the amount of hydrogen sulfide released during the period of agitation was measured. Agitation was accomplished by repositioning the inlet diffusion tube such that gas was bubbled from the bottom of the digestor, and by swirling the digestor by hand several times. The length of the agitation period was set arbitrarily at one hour.

4.7.5 Total Sulfides in Digested Manure.

Immediately after the cessation of agitation, the tops were removed from each digestor and 50-ml samples of the digestor contents were removed for pH determinations. The contents of each digestor then were acidified to a pH of approximately 1.0 by the addition of 60 - 100 mls of concentrated hydrochloric acid, depending on the original pH of the manure, and purged with nitrogen gas until tests showed that no more hydrogen sulfide was being released. The total sulfide content of the manure in each digestor was calculated from the weight of cadmium sulfide precipitate collected subsequent to the addition of acid. The pH of the manure after acidification was checked to ensure that a pH value nearly equal to 1.0 had been achieved.

4.7.6 Bench-scale Incubation Trial with Iron Treatments.

In a review on anaerobic corrosion of iron pipes in service in gas-field applications,Davis (33) suggested that one of the requirements for serious corrosion is the coupling of the anaerobic site of sulfate-reducing bacteria development (anode) to areas of more or less aeration (cathode). A trial was conducted, therefore, using the bench-scale digestors, in which the uppermost layers could remain aerobic while the lower layers became anaerobic, to evaluate the effect of metallic and ferrous iron on the amount of hydrogen sulfide released upon agitation of fermented manure. The digestors were filled at Installation C directly from a manure tanker and then transported to the Agricultural Engineering Laboratory at the Ellerslie Research Station. The raw manure was the same as that used in Laboratory

Trial No. III. After filling, treatments were applied to each of the three digestors as outlined in Table 9. At the laboratory, the digestors were allowed to remain undisturbed during the entire incubation period of thirty days. During incubation, the tops were left off the digestors, thereby simulating open manure tanks. At the end of incubation, tops were secured on the digestors and the digestors tipped over as shown in Figure 20. The contents of each digestor were purged for one hour with nitrogen gas supplied from a pressurized cylinder. Hydrogen sulfide released was collected in cadmium acetate solution and determined as outlined in Section 4.5.3.2. However, because of the larger volume of gas required to mix the digestor contents, a system of larger gas scrubbers was fabricated from 1/2-gallon glass bottles (Figure 20).

TABLE 9: DESCRIPTION OF BENCH-SCALE INCUBATION TRIAL.

Digestor	Manure Sample	Treatment	Description
1	C-1015 (400 lb)	Ferrous iron	$FeCl_2 . 4H_2O$ - 158 gm
2		Control	-
3		Metallic iron	3 ft section of 2 in. black iron pipe 2865 gm

4.8 Methods of Analysis.

4.8.1 Total Solids.

The total solids content of each manure and wastewater sample was determined, in duplicate, at both the Agricultural Engineering

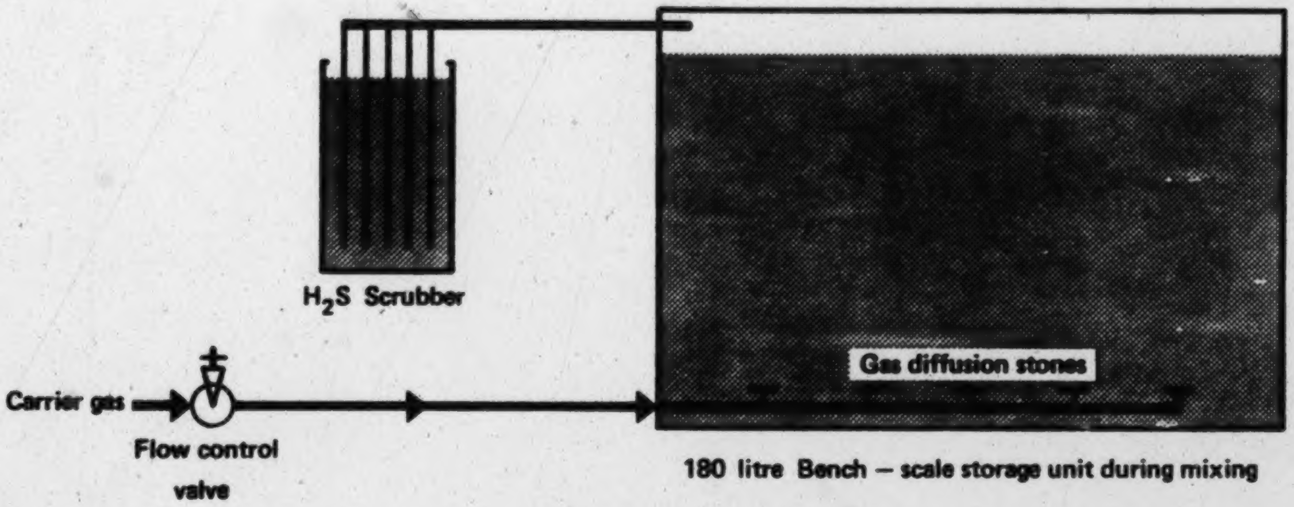
H$_2$S Scrubber
Carrier gas
Flow control valve
Gas diffusion stones
180 litre Bench – scale storage unit during mixing

Figure 20. Schematic of equipment used to monitor hydrogen sulfide released from manure incubated in bench-scale digestors.

Laboratory (AEL) and the Soil and Feed Testing Laboratory (SFTL) by drying the samples to constant weight in a forced air oven at 105 - 110°C.

4.8.2 pH.

Analyses of manure and wastewater samples for pH were conducted on all manure and wastewater samples at both the AEL and SFTL by the glass electrode method. The pH determinations were made on unblended samples at the AEL and on blended samples at the SFTL.

4.8.3 Color.

Only a very general description of color was attempted for each manure and wastewater sample. The colors were recorded as some combination of red, brown, black, green and amber, with the dominant color listed first.

4.8.4 Total Nitrogen.

Analyses of manure and wastewater samples for nitrogen were performed at the SFTL on the wet samples. The Kjeldahl method was employed according to the procedures used by the Laboratory for soil and feed samples. Nitrogen detected by this method includes all organic- and ammonia-nitrogen but not nitrate- or nitrite-nitrogen.

4.8.5 Total Sulfur.

Samples of manure, feces, and urine were prepared for analyses of total sulfur at the Soil Science Laboratory (SSL) as follows:

(a) Manure and wastewater samples: Approximately 5 grams of material was measured into a Kjeldahl flask and the weight recorded to the nearest milligram. The neck of the flask was washed down with a little distilled water, and the samples were digested to dryness with acid (20 ml-nitric acid plus 2 ml perchloric acid).

(b) Feces samples: Samples of feces were dried to constant weight in a forced air oven at 60°C (approximately 72 hours). The air dried samples were pulverized and 1.000-gram subsamples were weighed into Kjeldahl flasks. These samples then were digested to dryness with acid (12 ml nitric acid plus 2 ml perchloric acid).

(c) Urine samples: A 5-ml aliquot of each urine sample was pippeted into a Kjeldahl flask, and the samples were digested to dryness with acid (10 ml nitric acid plus 2 ml perchloric acid).

The acid digestion procedure described above was employed to oxidize all sulfur in the samples to sulfate-sulfur. The ash remaining in each of the flasks after digestion was dissolved in a reducing solution, in which all sulfate is reduced to sulfide. The sulfide was evolved as hydrogen sulfide, collected in a bismuth reagent, and its concentration determined photometrically. The procedure has been described in detail by Carson et al. (25).

4.8.6 Total Sulfate-Sulfur.

Total sulfate-sulfur analyses were performed only on samples of feces and urine. Samples of excreta were prepared for analysis as follows:

(a) Feces samples: Samples of feces were dried to constant weight in a forced air oven at 60°C. The dried samples then were prepared for sulfate analysis by shaking 5.000 gram subsamples with 50 ml of 2 N hydrochloric acid for 20 minutes, followed by filtering through No. 41 Whatman filter paper.

This method of extraction was recommended by Bird and Fountain (12).

(b) Urine samples: Samples of urine, which had been stored at $-20^{\circ}C$, were thawed and acidified to a pH of approximately 2 with hydrochloric acid. Subsamples of the acidified urine were filtered through No. 41 Whatman filter paper.

Subsamples of the filtrate from both feces and urine samples then were analyzed for sulfate-sulfur by the method previously described for total sulfur (i.e., reduction of sulfate to sulfide and photometric determination of the concentration of sulfide in a bismuth solution).

4.8.7 Water-Soluble Sulfate-Sulfur.

Samples of manure and wastewater were filtered through No. 42 Whatman filter paper. Subsamples of the filtrate then were analyzed for sulfate-sulfur exactly as described for total sulfur and total sulfate-sulfur determinations.

4.8.8 Sulfate-Reducing Bacteria.

The numbers of sulfate-reducing bacteria in manure samples were determined by personnel of the Soil Microbiology Laboratory, Department of Soil Science, University of Alberta. The most probable number (M.P.N.) technique was used, in which 10 tubes of each of three dilutions of the manure sample were scored for evidence of growth of sulfate-reducing bacteria after an incubation period of two weeks. An M.P.N. table then was used to arrive at the most probable number of organisms per gram of the original manure sample.

5. RESULTS AND DISCUSSION

5.1 Sulfur Status of Fresh Swine Excreta.

5.1.1 Sulfur and Nitrogen Excretion by Feeder Pigs.

Data on the intake and excretion of sulfur and nitrogen by feeder pigs receiving two different diets are given in Appendix H. From that data, the three-day sulfur-nitrogen balances for each group of pigs were calculated and are given in Table 10. Considering the overall means only for the various parameters listed in Table 10, the following observations may be made (In all cases throughout this discussion, the range of values recorded is indicated in parenthesis):

(1) Partition of sulfur excretion between the feces and urine - Approximately 71% (49 - 100) of the sulfur intake by the pigs was excreted. Of the sulfur which was excreted, 29% (18 - 40) was excreted in the feces and 71% (60 - 83) in the urine. The amount of sulfur excreted in the urine, expressed as a percentage of the total sulfur intake, was extremely variable (31 - 91%) whereas fecal sulfur excretion, expressed in the same manner, varied much less (17.5 - 23.5%).

(2) Forms of sulfur excreted - Of the sulfur excreted in the feces, 1.3% (0.9 - 2.0) was excreted as sulfate, the remainder being excreted as sulfur bound in C - S linkages (neutral or organic sulfur). On the other hand, nearly 100% (92 - 100) of the urinary sulfur was in the form of sulfate-sulfur. These results are in agreement with those reported for other classes of livestock (Section 2.2.4). Of the total sulfur excreted, 72% (61 - 80) was excreted as sulfate-sulfur. On the basis of availability of the substrate, then, sulfate reduction probably

TABLE 10: SULFUR AND NITROGEN EXCRETION BY FEEDER PIGS DURING A THREE-DAY PERIOD.

Parameter	Diets containing rapeseed 1	2	3	4	Treatment Mean	Diets not containing rapeseed 1	2	3	4	Treatment Mean	Over-all Mean
Nitrogen in feed: (gms)	107.27	94.11	113.95	109.58	106.23	125.64	98.54	113.21	104.94	110.58	108.40
Sulfur in feed: (gms)	11.03	9.71	11.89	11.47	11.03	10.62	8.36	9.75	9.07	9.45	10.24
Nitrogen excretion:											
Feces											
(gms)	21.12	14.33	20.97	16.64	18.26	23.12	15.70	17.84	14.18	17.71	17.98
(% of feed N)	19.69	15.23	18.40	15.19	17.19	18.40	15.93	15.76	13.51	16.02	16.59
Urine											
(gms)	39.36	39.51	46.56	40.84	41.57	51.81	35.43	49.47	37.89	43.65	42.61
(% of feed N)	36.69	41.98	40.86	37.27	39.13	41.24	35.95	43.70	36.11	39.47	39.31
Total excretion:											
(gms)	60.48	53.84	67.53	57.48	59.83	74.93	51.13	67.31	52.07	61.36	60.60
(% of feed N)	56.38	57.21	59.27	52.45	56.32	59.64	51.89	59.46	49.62	55.49	55.90
Nitrogen digestibility: (%)	80.31	84.77	81.60	84.81	82.81	81.60	84.07	84.24	86.49	83.98	83.41
Nitrogen retention: (%)	43.62	42.79	40.73	47.55	43.68	40.36	48.11	40.54	50.38	44.51	44.10

Continued

TABLE 10: Continued

Parameter	Diets containing rapeseed 1	2	3	4	Treatment Mean	Diets not containing rapeseed 1	2	3	4	Treatment Mean	Over-all Mean
Sulfur excretion:											
Feces											
(gms)	2.54	1.70	2.08	2.21	2.13	2.49	1.83	2.27	1.90	2.12	2.12
(% of feed S)	23.03	17.51	17.49	19.27	19.31	23.45	21.89	23.28	20.95	22.43	20.75
(% of total S excreted)	39.44	18.42	35.86	17.43	24.94	37.73	32.05	33.98	38.62	35.51	29.34
Urine											
(gms)	3.90	7.53	3.72	10[illegible]	6.41	4.11	3.88	4.41	3.02	3.85	5.13
(% of feed S)	35.36	77.55	31.29	91[illegible]8	58.11	38.70	46.41	45.23	33.30	40.74	50.10
(% of total S excreted)	60.56	81.58	64.14	82.57	75.06	62.27	67.95	66.02	61.38	64.49	70.66
Total excretion:											
(gms)	6.44	9.23	5.80	12.68	8.54	6.60	5.71	6.68	4.92	5.97	7.26
(% of feed S)	58.39	95.06	48.78	110.55	77.43	62.15	68.30	68.51	54.24	63.17	70.85
Sulfur digestibility: (%)	76.97	82.49	82.51	80.73	80.69	76.55	78.11	76.72	79.05	77.57	79.25
Sulfur retention: (%)	41.61	4.9	51.22	-10.55	22.57	37.85	31.70	31.49	45.76	36.83	29.15

Continued

TABLE 10: Continued

Parameter	Diets containing rapeseed					Diets not containing rapeseed					Over-all Mean
	1	2	3	4	Treatment Mean	1	2	3	4	Treatment Mean	
Sulfate excretion:											
Feces											
(gms)	0.028	0.019	0.024	0.033	0.026	0.023	0.027	0.033	0.038	0.030	0.028
(% of fecal S)	1.09	1.14	1.14	1.48	1.21	0.93	1.50	1.46	1.99	1.44	1.32
Urine											
(gms)	4.03	7.33	3.80	9.65	6.20	4.01	4.29	4.89	3.41	4.15	5.18
(% of urinary S)	100	97.34	100	92.17	96.79	97.6	100	100	100	100	100
Total excretion:											
(gms)	4.06	7.35	3.82	9.68	6.23	4.03	4.32	4.92	3.45	4.18	5.20
(% of total S excreted)	63.01	79.62	65.93	76.36	72.90	61.11	75.60	73.70	70.08	70.02	71.69
Nitrogen:Sulfur ratio											
feed	9.73	9.69	9.58	9.55	9.63	11.83	11.79	11.61	11.57	11.70	10.59
feces	8.32	8.43	10.08	7.53	8.57	9.29	8.58	7.86	7.46	8.35	8.46
urine	10.09	5.25	12.52	3.90	6.49	12.61	9.13	11.22	12.54	11.34	8.31
Total excretion	9.39	5.83	11.64	4.53	7.01	11.35	8.95	10.08	10.58	10.28	8.35

would be the primary source of sulfides if these excreta were fermented anaerobically.

(3) Variations in sulfur and nitrogen digestion and retention - The digestion[a] and retention[b] of dietary nitrogen by the feeder pigs were 84% (80.5 - 86.5) and 44% (40.5 - 50.5) respectively, whereas the digestion and retention of dietary sulfur were only 79% (76.5 - 82.5) and 29% (-10.5 - 51.0), respectively. These differences in sulfur and nitrogen digestibility and retention are reflected in the generally lower nitrogen:sulfur (N:S) ratios of the feces (8.5) and urine (8.3) than of the feed (10.6). Because of the very large variations in sulfur rentention by different animals, the N:S ratio of the urine samples varied widely (3.9 - 12.6); On the other hand, lesser variations were noted for sulfur digestibility and consequently, lesser variations were recorded for the N:S ratios of the feces (7.5 - 10.1). The observed variations in nitrogen and sulfur retention indicate that, whereas there is an apparently close relationship between the nitrogen composition of the feed and excreta for a given class of swine, such a relationship does not appear to exist between the sulfur composition of the feed

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[a] Nitrogen or sulfur digestibility is calculated as the difference between the nitrogen or sulfur consumed in the feed and the nitrogen or sulfur excreted in the feces. The percent digestibility of a given dietary constituent, then, represents the percent of the constituent consumed which is absorbed by the animal.

[b] Nitrogen or sulfur retention is calculated as the difference between the nitrogen or sulfur which is digested and the nitrogen or sulfur excreted in the urine. The percent retention of a given dietary constituent, then, represents the percent of the constituent consumed which is retained in the animal's body.

and excreta. Consequently, models used to predict the nutrient composition of swine manure on the basis of nutrient intake in the feed would not likely be as reliable in the case of sulfur as in the case of nitrogen.

5.1.2 Effect of Diet on Sulfur and Nitrogen Excretion by Feeder Pigs.

Comparisons between the various parameters presented in Table 10 for the two treatments, rapeseed versus no rapeseed in the diet, were made using analysis of variance procedures (134). The following observations may be made with regard to the results of this analysis:

(1) Animals on the rapeseed diets excreted a higher percentage of their total sulfur intake than did animals not receiving rapeseed. This increase was totally the result of increased urinary sulfur excretion. Sulfur excretion in the feces was actually slightly higher for animals on the diets without rapeseed. None of the reported differences were significant as indicated by the calculated F-values (Table 11).

(2) Of the total sulfur excreted, a larger proportion was excreted via the urine by animals on the rapeseed diets than by the others. This difference between the two treatments in the partition of sulfur excreted via the feces and urine was not significant as indicated by the calculated F-value (Table 11).

(3) Nitrogen excretion in the feces and the urine did not differ appreciably between the two treatments. Consequently, any differences in the N:S ratios between the two treatments were due to differences in sulfur excreted. No significant differences were found to exist between the N:S ratio of the

TABLE 11: ANALYSIS OF VARIANCE - SULFUR AND NITROGEN EXCRETION BY FEEDER PIGS.

Parameter	Source of Variation	Degrees of Freedom	Mean Squares	F^a
Sulfur(S) intake	Between Treatments	1	4.96	5.45
	Within Treatments	6	0.91	
Nitrogen(N) intake	Between Treatments	1	37.93	0.36
	Within Treatments	6	104.88	
N:S ratio in feed	Between Treatments	1	8.51	851**
	Within Treatments	6	0.01	
Total S excretion (% of S intake)	Between Treatments	1	443.72	0.98
	Within Treatments	6	454.05	
Urinary S excretion (% of S intake)	Between Treatments	1	645.12	1.37
	Within Treatments	6	470.74	
Fecal S excretion (% of S intake)	Between Treatments	1	18.82	4.58
	Within Treatments	6	4.10	
Partition of S excretion between feces and urine	Between Treatments	1	121.91	1.72
	Within Treatments	6	70.81	
N:S ratio in total excreta	Between Treatments	1	11.45	1.97
	Within Treatments	6	5.81	
N:S ratio in urine	Between Treatments	1	0.17	0.18
	Within Treatments	6	0.93	
N:S ratio in feces	Between Treatments	1	23.60	2.48
	Within Treatments	6	9.52	

** significant at the 0.01 level of probability

[a] significant F values are 13.75 at the 0.01 level of probability, and 5.99 at the 0.05 level of probability.

feces, the urine, or the total excretion for animals receiving the two different diets. Neither were any definite trends evident.

(4) The sulfur composition of the diets containing rapeseed was 26% (0.29% compared to 0.23%) higher than that of the diets not containing rapeseed. However, animals being fed rapeseed consumed 7.5% (3802 grams compared to 4110) less feed than those not receiving rapeseed so that the actual difference in sulfur intake by animals in the two treatments was reduced to only 12% (11.03 grams compared to 10.24 grams). This difference was not significant as indicated in Table 11 by the calculated F-value.

(5) The combined effects of a slightly higher sulfur intake and a slightly lower nitrogen intake by animals on the rapeseed diets resulted in there being a highly significant difference in the N:S ratio of the feed consumed by each group of animals.

(6) The observed differences in sulfur excretion by the two groups of animals are in agreement with the results of other research as reported in Section 2.2.4.

An increase in the sulfur content of the ration (rapeseed diets higher in sulfur content than the other diets) apparently resulted in more sulfur being excreted, the increase largely confined to an increase in urinary sulfur excretion.

5.2 Sulfur Status of Swine Manure and Wastewaters.

5.2.1 Sulfur and Nitrogen Composition of Liquid Swine Manure, and Lagoon Supernatants and Sludge.

Because of the combined restrictions of time and resources, only ten samples of liquid manure and two samples of lagoon contents were collected for this investigation. A description of the samples and the code used to identify each are given in Table 12. The results of the analyses of the samples for total solids, pH, color, total nitrogen, total sulfur and water-soluble sulfate-sulfur are given in Appendix I.

Mean values for the total nitrogen, total sulfur, and water-soluble sulfate-sulfur contents of each sample are presented in Table 13. Table 13 also gives the calculated values for the N:S ratio of each sample and the percentage of total sulfur existing as sulfate-sulfur in each sample. The following observations may be made on the basis of the tabulated data:

(1). The total nitrogen, total sulfur, and sulfate-sulfur content of the manure samples varied considerably, even among samples collected from the same pig production unit.

(2) Considered as a group, the manure samples from any one installation had N:S ratios distinctly different from the N:S ratios of samples from the other two installations. These observed differences are most probably due to differences in the classes of swine from which the manure originated. Manure from Installation C, which was solely from feeder pigs, had the lowest N:S ratios while manure from Installation B was solely from sows and had the highest N:S ratios. Manure from Installation A originated partly from sows and partly from feeder pigs and had N:S ratios intermediate to those of the other two installations. Since sows and feeder pigs receive different rations and probably retain different proportions of

TABLE 12: MANURE AND WASTEWATER SAMPLES COLLECTED FROM INSTALLATIONS A,B, AND C.

Code*	Description
A-0501 A-0528 A-0707 A-0811 A-1108	"Sour" liquid manure from underfloor pits.
B-0522-L	Lagoon supernatant
B-0522-S	Lagoon sludge
B-0522 B-0529	Chemically-treated liquid manure
C-0523 C-0907 C-1015	Fresh liquid manure from collection tank.

* The first part of each sample code refers to the Installation from which the sample was collected. The next four digits denote the month and day of sampling. Further identifying codes were attached in cases where the Installation and date of sample were insufficient to describe the sample uniquely.

TABLE 13: SULFUR AND NITROGEN COMPOSITION OF MANURE AND WASTE WATER SAMPLES

Sample	Total N		Total S		SO_4-S	N:S	$\frac{SO_4\text{-S}}{\text{Total S}}$ X 100
	%w.b.	%d.b.	ppm w.b.	%d.b.	ppm w.b.	ratio	
A-0501	0.267	5.79	282	0.612	123	9.47	43.62
A-0528	0.338	3.55	385	0.405	120	8.78	31.17
A-0707	0.270	4.04	285	0.427	62	9.47	21.75
A-0811	0.260	4.34	251	0.340	47	10.36	18.72
A-1108	0.364	4.39	331	0.470	46	11.00	13.90
B-0522-L	0.037	16.82	75	3.409	66	4.93	88.00
B-0522-S	0.256	3.40	443	0.589	69	5.78	15.58
B-0522	0.084	9.88	116	1.365	54	7.24	46.55
B-0529	0.099	9.00	145	1.318	52	6.83	35.86
C-0523	0.308	5.25	268	0.457	156	11.49	58.21
C-0907	0.240	7.89	165	0.543	74	14.54	44.85
C-1015	0.307	7.89	252	0.648	136	12.18	53.97

their sulfur and nitrogen intake, the existence of such a relationship would appear possible.

(3) In agreement with the assumption that the red color of the lagoon from which samples B-022-L and B-022-S were collected was due to the presence of photosynthetic sulfur bacteria, the proportion of sulfur existing as sulfate in the lagoon supernatant was very high while the proportion of sulfate in the sludge was very low. Sulfate-reducing bacteria would be expected to be very active in the sludge, reducing sulfate to hydrogen sulfide which, in turn, would be oxidized to sulfate by purple sulfur bacteria in the red-colored supernatant liquid above the sludge.

(4) The percentage of sulfur existing as sulfate in the manure samples from Installation A showed a consistent decrease throughout the sampling period from May to November. Conversely, the N:S ratio of the same manure samples exhibited a relatively consistent increase over the same period. As noted in Section 4.2.1, the pits from which these samples were collected could not be drained completely because of problems experienced with emptying the adjoining lagoons. Consequently, there was a gradual build-up of rather "sour" manure in the bottom of the pits, some of which was included in the samples collected for analysis. This sludge accumulation no doubt provided an excellent environment for sulfate reduction. Rampant activity of sulfide-producing bacteria and, in particular, sulfate-reducing bacteria could account for the decreased proportions

of sulfate-sulfur in the manure samples and a generally greater loss of sulfur (as hydrogen sulfide) than nitrogen from the pits to give the higher N:S ratios.

5.2.2 Effect of Aerobic and Anaerobic Storage on the Sulfur Status of Swine Manure.

An attempt was made during this investigation to gain some insight into the sulfur transformations occurring in manure during aerobic and anaerobic storage. Two samples of manure were incubated both aerobically and anaerobically (A-0707 and C-0907) while two other samples (A-0811 and C-0907-b) were subjected only to anaerobic incubation. Sample C-0907-b was actually a blended subsample of Sample C-0907. the codes assigned to identify each of the incubated manure samples are given in Table 14.

TABLE 14: IDENTIFICATION CODES OF AEROBICALLY AND ANAEROBICALLY INCUBATED MANURE SAMPLES.

Sample Incubated	Aerobically-incubated samples	Anaerobically incubated samples
A-0707	A-0707-a	A-0707-n
A-0811	-	A-0811-n
C-0907	C-0907-a	C-0907-n
C-0907-b	-	C-0907-bn

All samples of manure were analyzed before and after incubation for total solids, pH, color, total nitrogen, total sulfur, and water-soluble sulfate-sulfur. These data are given in Appendix I. Changes in the properties and constituents of the manure samples during incubation are shown in Table 15. The range of values obtained for each parameter by analysis of multiple subsamples of each manure sample are included in parenthesis after the mean values.

A survey of the data in Table 15 indicates that there was very poor agreement among the results of multiple analyses for the same constituent in a given manure sample. Furthermore, as shown in Appendix I, there was generally considerable variation among the results obtained by personnel of the three different laboratories. In the case of the total solids and total sulfur determinations, the variations are probably due primarily to the difficulties that are experienced when small representative subsamples of manure (in the order of 1 to 50 grams) must be collected from larger bulk samples of non-homogeneous material. The close duplication of results for total solids determinations within each given laboratory, but the wide variation in the mean values obtained by each, suggests that a slight difference in technique also may have been responsible for some of the observed discrepancy. In the case of pH determinations, the reported differences between the measured values at the two laboratories are most probably due to sample quality changes during storage and handling. In particular, the blending process results in a loss of volatile manure constituents and hence a change in pH.

Because of the nature of the data which was collected, and because only a very limited number of samples were analyzed, a rigid statistical analysis of the data was not performed. However, careful examination of the data in Table 15 may reveal the following trends:

TABLE 15: CHANGES IN THE SULFUR AND NITROGEN STATUS OF MANURE DURING STORAGE.

Parameter	Sample	Before incubation	After aerobic incubation	After anaerobic incubation
N:S ratio	A-0707	9.47(8.88-10.00)	7.37(6.06-10.85)	11.36(10.00-12.45)
	A-0811	10.36(8.31-12.22)	-	11.61(10.75-13.24)
	C-0907	14.54(13.68-15.25)	10.82(10.00-11.49)	13.86(13.63-14.00)
	C-0807-b	14.54(13.68-15.25)	-	15.82(14.10-17.07)
Total N (% w.b.)	A-0707	0.270(0.270)	0.210(0.208-0.212)	0.259(0.254-0.264)
	A-0811	0.260(0.257-0.264)	-	0.274(0.271-0.278)
	C-0907	0.240(0.238-0.241)	0.210(0.202-0.216)	0.244(0.244-0.245)
	C-907-b	0.240(0.238-0.241)	-	0.250(0.244-0.256)
Total S (ppm w.b.)	A-0707	285(270-304)	285(196-343)	228(212-254)
	A-0811	251(216-276)	-	236(210-252)
	C-0907	165(158-174)	194(188-202)	176(175-179)
	C-0907-b	165(158-174)	-	158(150-173)
SO_4-S (ppm w.b.)	A-0707	62(60-64)	54(54)	54(50-58)
	A-0811	47(46-48)	-	50(46-54)
	C-0907	74(70-78)	67(66-68)	82(80-84)
	C-0907-b	74(70-78)	-	144(144)
%SO_4-S	A-0707	21.75(19.74-23.70)	18.95(15.74-27.55)	23.68(19.69-27.36)
	A-0811	18.72(16.67-22.22)	-	21.19(18.25-25.71)
	C-0907	44.85(40.23-49.37)	34.54(32.67-36.17)	46.59(44.69-48.00)
	C-0907-b	44.85(40.23-49.37)	-	91.14(83.24-96.00)

(1) The total nitrogen composition of the aerobically-incubated samples was less than that of the anaerobically-incubated samples. Ammonia-nitrogen probably would escape more rapidly from the aerobically-incubated samples because of their relatively high pH than from the anaerobically-incubated samples whose pH values were very much lower.

(2) The mean total sulfur composition of the anaerobically-incubated manure samples was less than that of the aerobically-incubated manure samples. Manure incubated anaerobically would be expected to decrease in total sulfur content due to losses of sulfur as hydrogen sulfide and other volatile sulfur compounds. A similar escape of sulfur from aerobic manure would not be expected.

(3) The observed larger N:S ratios of anaerobically-incubated manure as compared to aerobically-incubated manure are in agreement with the above-mentioned differences in the total sulfur and nitrogen contents of each.

(4) The general trend of increasing amounts of sulfate and increasing proportions of total sulfur existing as sulfur in anaerobic manure as compared to aerobic manure is surprising and difficult to explain. Other researchers (95) have demonstrated large increases in available sulfate upon aerobic incubation of livestock feces whereas decreases were observed in this investigation. In the case of anaerobically-incubated manure, a decrease in the sulfate composition might have been expected as a result of sulfate reduction. The observed discrepancies may be due to inadequacies of the method employed for determination of sulfate-sulfur. A filtrate of the anaerobic

manure could have contained significant amounts of sulfides which would be undistinguishable from sulfates by the method of sulfate analysis described in Section 4.8.7. Furthermore, since no salt solution was used for extraction of sulfates into water solution, the double blending of sample C-0907-nb could account for a relatively larger release of sulfates and hence the larger recorded value of sulfate in that sample. Finally, even a water-filtrate of a manure sample contains some organic matter as evidenced, for example, by the substantial BOD exerted by manure solutions. Sulfur in the dissolved organic matter likely is easily reducible and would be measured as sulfate by the method of sulfate analysis employed in this investigation. The totally aerated solution probably would have contained less dissolved organic matter (lower BOD) than the unincubated (untreated) or anaerobically-incubated manure solutions and hence would have appeared to contain less "sulfate".

5.3 Chemical Control of Sulfides From Anaerobic Swine Manure.

Eight chemical treatments were evaluated for their effects on the production and release of sulfides from anaerobically fermented swine manure. To provide a common basis for comparison, an untreated manure sample was incubated with each group of chemically-treated samples.

The raw manure samples used in each of the four incubation trials were identified in Table 5, and the characteristics of those samples are summarized in Table 16. Trials I and IV were conducted with manure from Installation A (Manure A) while Trials II and III were conducted with manure from Installation C (Manure C). Treatments were allotted during the trials in such a manner that each chemical was applied once to the manure from each of the two installations.

As indicated in Table 16, samples of manure A were very much different, both physically and chemically, from samples of manure C. On the other hand, the two samples of Manure A were very much alike as were the two samples of Manure C. For purposes of the ensuing discussion, therefore, the two samples from the same installation are assumed to be identical, thereby enabling comparisons to be made between chemical treatments.

Data were collected for each chemical treatment during each incubation trial as follows:

(1) The rate of sulfide evolution, expressed as mg H_2S/hr, and calculated as the sulfide collected during each particular collection period divided by the length of the collection period in hours. Data are tabulated for each trial in Appendix J.

(2) The cumulative evolution of sulfides at various times throughout the incubation period, expressed as mg H_2S, and calculated as the total production of sulfides from the beginning of incubation to the time of analysis. Data are tabulated for each trial in Appendix J. The data for the two trials with each treatment are plotted, together with data for the two corresponding controls, in Figures 21a to 28a.

TABLE 16: DESCRIPTION AND CHARACTERISTICS OF MANURE SAMPLES USED IN INCUBATION TRIALS WITH THE CHEMICAL TREATMENTS.

Characteristics	Trial I	 II	 III	 IV	Average for two samples from each Installation A	 C
Sample code	A-0811	C-0907	C-1015	A-1108	-	-
Total Solids (%)	5.99	3.04	3.89	8.30	7.14	3.46
pH	6.7	6.6	6.5	6.6	6.65	6.55
color	Black-Green	Green-Brown	Green-Brown	Black-Green	Black-Green	Green-Brown
Total Nitrogen						
(% w.b.)	0.260	0.240	0.307	0.364	0.312	0.274
(% d.b.)	4.34	7.89	7.89	4.39	4.36	7.89
Total Sulfur						
(ppm w.b.)	251	165	252	331	291	208
(% d.b.)	0.340	0.543	0.648	0.470	0.405	0.596
Water-soluble sulfate-sulfur (ppm w.b.)	47	74	136	46	46	105
N:S ratio	10.36	14.54	12.18	11.00	10.68	13.36
% Sulfate-sulfur	18.72	44.85	53.97	13.90	16.36	49.41

For purposes of comparing each treatment to its corresponding control, the total sulfide production was subdivided into that produced prior to the time of chemical additions and that produced after the time of chemical additions. These values are tabulated in Table 17.

(3) The rate of carbon dioxide evolution, expressed as mg CO_2/hr, and calculated as the total carbon dioxide collected during each particular collection period divided by the length of that collection period in hours. Data are tabulated for each trial in Appendix J. The data for the two trials with each treatment are plotted, together with data for the two corresponding controls, in Figures 21b to 28b.

(4) Sulfide released upon agitation, expressed as mg H_2S, and calculated as the quantity of sulfide released from the digested manure when agitated for one hour at the termination of incubation. Data are presented in Table 17 for each trial.

(5) The total sulfide content of the digested manure, expressed as mg H_2S, and calculated as the amount of sulfide released from the manure by acidification to a pH nearly equal to 1.0. Data are presented in Table 17 for each trial.

(6) The total production of sulfides, expressed as mg H_2S, and equal to the sum of the sulfides released during incubation, the sulfides released upon agitation, and the total sulfide content of the digested manure. The value calculated accounts not only for the sulfide produced during incubation but also for the sulfide in the manure prior to incubation. Data are

TABLE 17: EVOLUTION OF SULFIDES FROM CHEMICALLY-TREATED MANURE.

Trial	Treatment	Sulfides Evolved (mg H_2S)				
		A	B	C	D	E
I	Control	70.8	132.4	11.6	165.6	380.4
	Ferrous + powdered iron	62.5	12.3	0.0	255.8	330.6
	Ferric iron	84.7	46.3	3.3	20.8	155.1
	Powdered iron	62.5	21.2	0.0	247.2	330.9
	Lime	75.3	25.9	0.0	185.6	286.8
	Nitrate	72.9	95.8	4.5	-	-
II	Control	57.4	89.4	14.4	54.2	215.4
	Ferrous + rod iron	58.3	20.1	5.9	125.5	209.8
	Powdered iron	60.9	44.4	2.6	159.5	267.4
	Lime	36.3	55.7	0.0	74.4	166.4
III	Control	39.4	84.5	34.9	62.6	221.4
	Ferric iron	37.0	25.1	7.3	58.0	127.4
	Iron rod	38.9	80.9	21.2	79.4	220.4
	Nitrate	41.5	33.1	4.7	>56.2	>135.5
	Ammonium persulfate	40.1	0.0	0.0	4.7	44.8
	Potassium permanganate	38.0	39.4	25.3	65.9	168.6
IV	Control	68.9	99.1	17.2	143.5	328.7
	Iron rod	69.2	87.1	9.9	156.2	322.4
	Ammonium persulfate	68.9	5.9	0.0	2.5	77.3
	Potassium permanganate	63.0	27.8	5.4	35.2	131.4

A = Sulfides released between beginning of incubation and time of chemical additions.
B = Sulfides released between time of chemical additions and end of incubation.
C = Sulfides released by agitation at end of incubation.
D = Total sulfides in digested manure at end of incubation.
E = Total sulfide production to end of incubation = A + B + C + D.

TABLE 18: PERCENT REDUCTIONS IN SULFIDES EVOLVED FROM CHEMICALLY TREATED MANURE COMPARED TO CORRESPONDING CONTROLS.

Treatment	Sulfide released after chemical additions*		Sulfide released upon agitation*	
	Manure A	Manure C	Manure A	Manure C
Ferrous iron	91	78	100	59
Ferric iron	65	70	72	79
Powdered iron	84	50	100	82
Iron rod	12	4	42	39
Lime	80	38	100	100
Nitrate	28	61	61	87
Ammonium persulfate	94	100	100	100
Potassium permanganate	72	53	69	28

* expressed as a percent of the sulfide released during the same period by the corresponding control.

TABLE 19: CHANGES IN pH AND COLOR OF MANURE SAMPLES DURING INCUBATION.

	pH		Color	
Treatment	Before Incubation	After Incubation	Before Incubation	After Incubation
Ferrous & metallic iron				
Manure A_a	6.7	8.0	Black-green	Black
Manure C_a	6.6	7.0	Green-brown	Black
Ferric iron				
Manure A_a	6.7	7.75	Black-green	Black
Manure C_b	6.5	6.5	Green-brown	Black
Iron powder				
Manure A_a	6.7	8.0	Black-green	Black
Manure C_a	6.6	7.2	Green-brown	Black
Iron rod				
Manure A_b	6.65	6.6	Black-green	Brown-green
Manure C_b	6.5	7.0	Green-brown	Green-brown
Lime				
Manure A_a	6.7	11.9	Black-green	Green
Manure C_a	6.6	10.1	Green-brown	Green-brown
Nitrate				
Manure A_a	6.7	7.7	Black-green	Brown-green
Manure C_b	6.5	8.9	Green-brown	Green-brown
Ammonium persulfate				
Manure A_b	6.65	5.5	Black-green	Amber
Manure C_b	6.5	6.1	Green-brown	Amber
Potassium permanganate				
Manure A_b	6.65	7.0	Black-green	Brown-green
Manure C_b	6.5	7.35	Green-brown	Green-brown
Control				
Manure A_a	6.7	7.7	Black-green	Brown-green
Manure A_b	6.65	6.55	Black-green	Brown-green
Manure C_a	6.6	7.0	Green-brown	Green-brown
Manure C_b	6.5	7.1	Green-brown	Green-brown

* Subscripts a and b are attached to permit the matching of each treatment to the correct corresponding control.

TABLE 20: COUNTS OF SULFATE-REDUCING BACTERIA IN CHEMICALLY-TREATED MANURE SAMPLES.

Treatment	X^a	P^b(%)	Number of organisms in 1 gram of manure
Control			
Manure C_a*	16.2	30.20	1.62×10^6
Manure C_b	0.792	10.73	0.79×10^6
Lime			
Manure C_a	0	-	0
Nitrate			
Manure C_b	0.493	14.99	493
Ammonium persulfate			
Manure C_b	0.139	0.32	13.9
Potassium permanganate			
Manure C_b	100.0	100.0	100×10^6

[a] The value read off the M.P.N. table for "X" is the most probable number of organisms per unit volume in the middle dilution of the three dilutions of manure which were scored for growth. This number multiplied by the reciprocal of the middle dilution gives the most probable number of organisms per gram of the original manure.

[b] The value read off the M.P.N. table for "P" indicates the percentage of time that the same answer for "X" would be recorded if an infinite number of analyses were performed on the same sample.

* Subscripts a and b are attached to permit the matching of each treatment to the correct corresponding control.

presented in Table 17 for each trial.

(7) The percent reductions in sulfide production from treated manure compared to corresponding controls, calculated from data given in Table. 17. The two parameters for which percent reductions were calculated are the amount of sulfide released during the incubation period after the time of chemical additions, and the sulfides released upon agitation of the digested manure. These data are presented in Table 18.

(8) Changes in pH of the manure during digestion, the pH being measured at the beginning and end of each incubation trial. Data are given in Table 19.

(9) Changes in the color of the manure during digestion, evaluated at various times throughout the trials. The colors of the manure before and after digestion are tabulated for each trial in Table 19.

(10) In several trials with chemical treatments, data were collected on the numbers of sulfate-reducing bacteria in the manure about one week after the time of chemical additions. These data are presented in Table 20.

5.3.1 Precipitation by Iron.

The expected effect of adding iron to anaerobically fermenting manure is a reduction in the amount of sulfide released during the fermentation process. Sulfides produced should be bound as insoluble iron sulfide and so should not be released from the manure solution. However, the total sulfide produced from the manure should not be affected adversely since the bacteria responsible for sulfide production are unaffected by low concentrations of iron, both soluble and insoluble, in the media. In other words, the concentration of total soluble sulfides in the media should be diminished and the concentration of total insoluble sulfides should be increased relative to an untreated control.

Examination of Figures 21a to 24a, and of the data presented in Table 18, indicates that iron added in all four forms did reduce the amount of sulfides released from anaerobically fermented manure. This reduction was low and almost non-existent in the case of iron added as an iron rod, but was 50% or more for iron added either in ionic forms or as finely powdered metallic iron. Regardless of the form in which iron is added to a sulfide-containing solution, it probably is converted first to the ferrous form before being precipitated as iron sulfide. In the case of metallic iron, this conversion to the ferrous form involves a slow and difficult process of oxidation which requires some form of catalysis for the reaction to occur at all. In an anaerobic manure solution, the catalytic effect is exerted quite likely by sulfate-reducing bacteria that serve to depolarize the electrochemical corrosion cells. This bacterial corrosion process is no doubt very dependent upon the ease with which the bacteria can come in contact with the zones of corrosion, and hence will occur to a much greater extent if the metal to be corroded has a large surface area. Corrosion of iron rods added to manure during fermentation was evident by deposits of iron sulfide and by pitting of the rods, but because of the relatively small surface of exposure, the rate of corrosion was much less than that of powdered iron, and probably did not provide sufficient ferrous iron for precipitation of the sulfides produced.

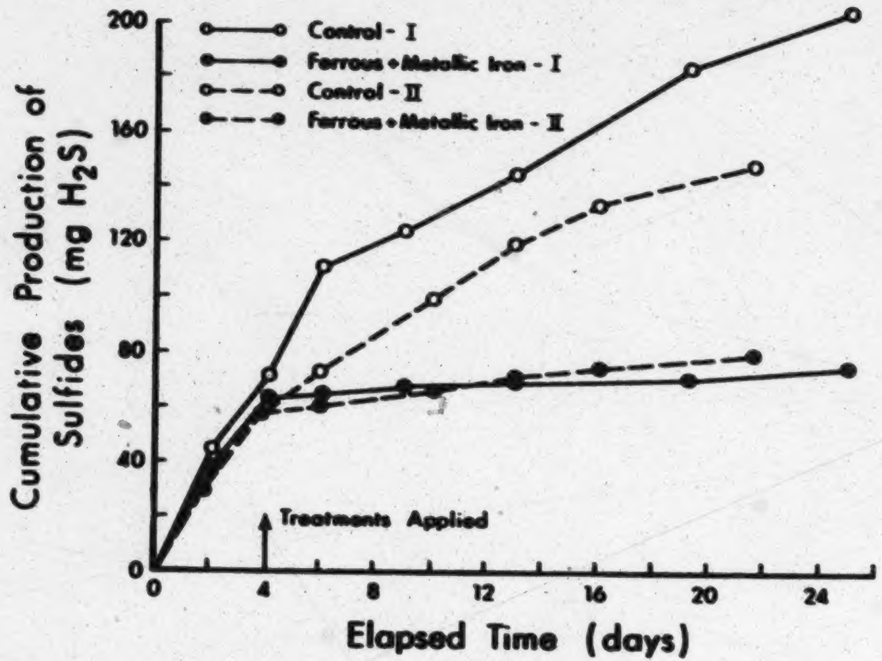

Figure 21a: Hydrogen sulfide production from manure treated with ferrous and metallic iron.

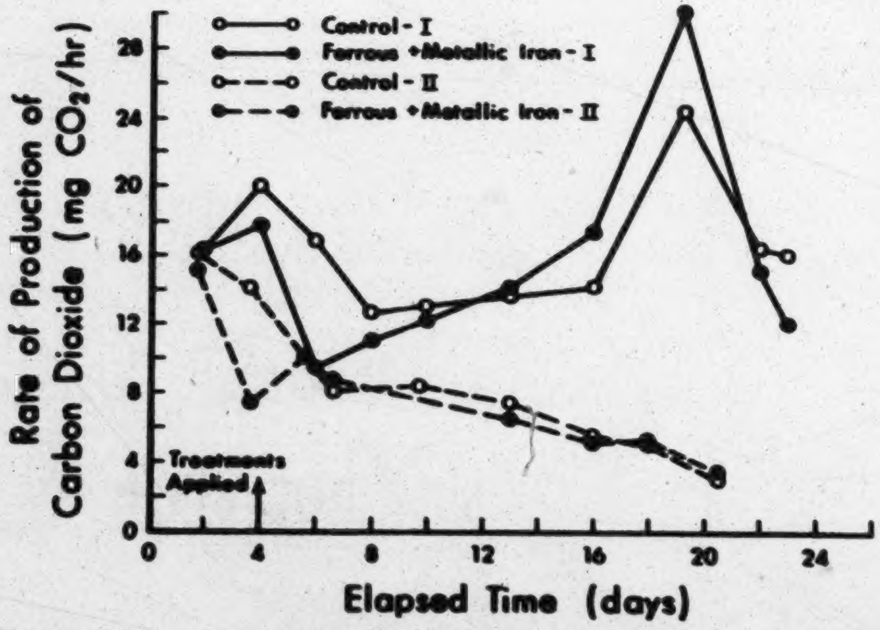

Figure 21b: Carbon dioxide production from manure treated with ferrous and metallic iron.

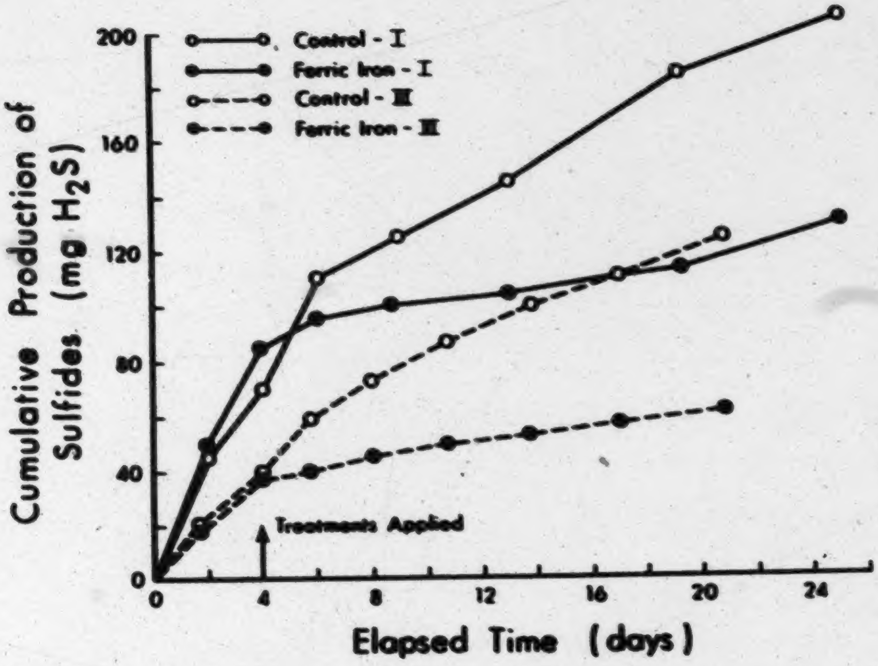

Figure 22a. Hydrogen sulfide production from manure treated with ferric iron.

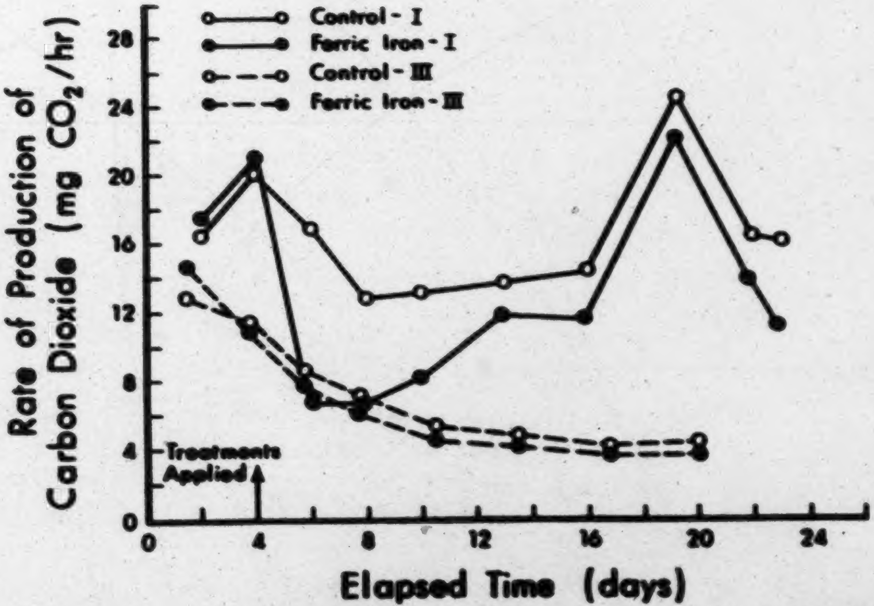

Figure 22b. Carbon dioxide production from manure treated with ferric iron.

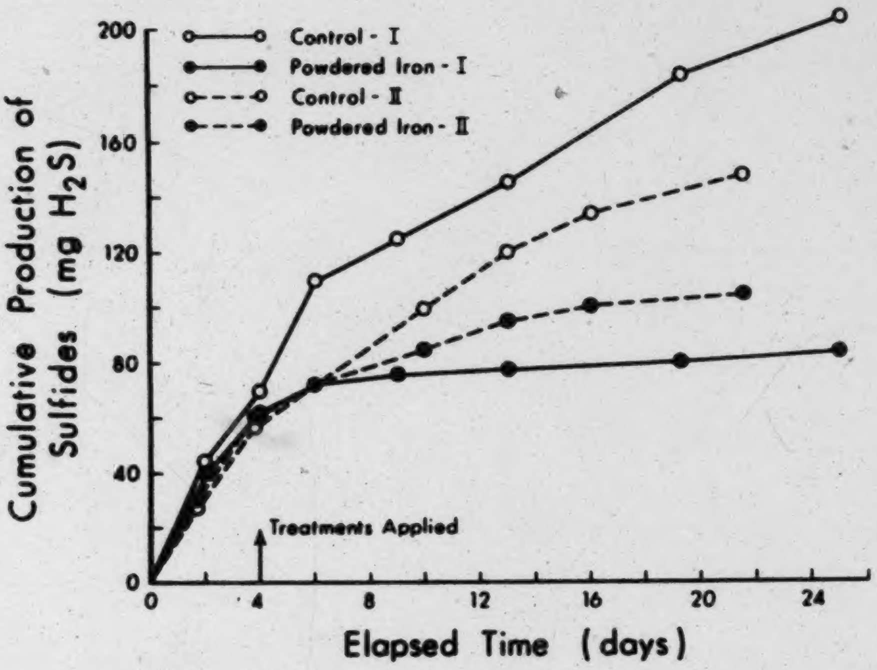

Figure 23a. Hydrogen sulfide production from manure treated with metallic iron added as a powder.

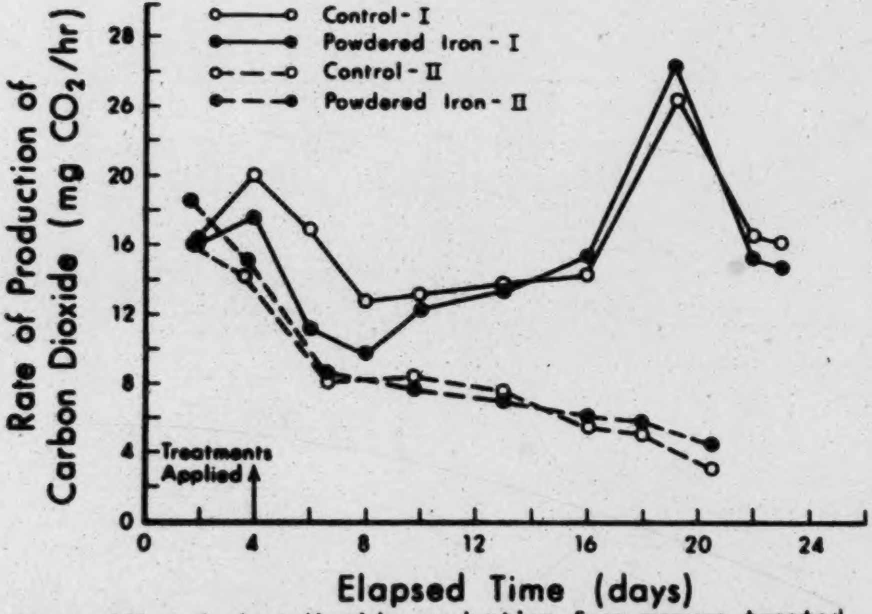

Figure 23b. Carbon dioxide production from manure treated with metallic iron added as a powder.

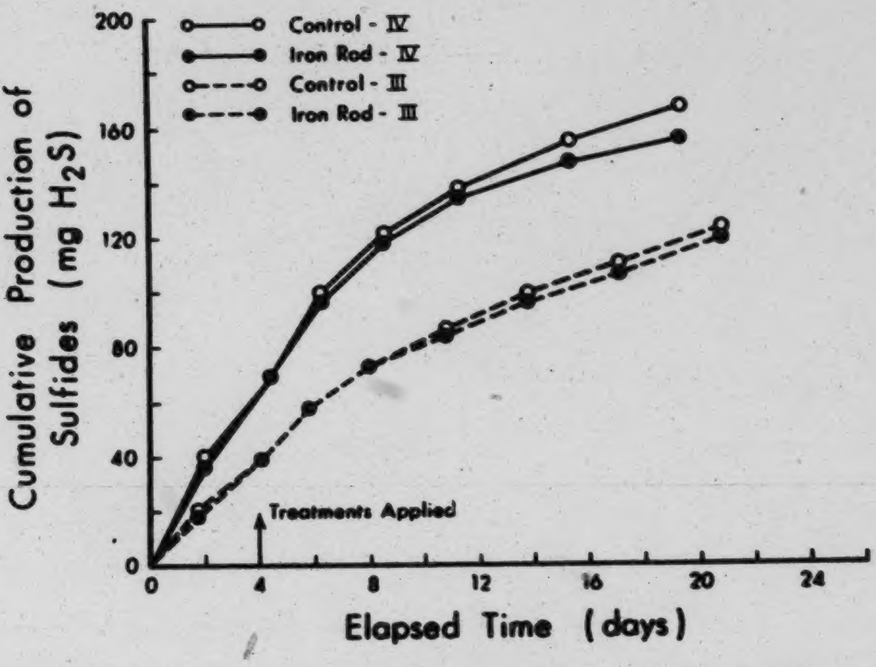

Figure 24a. Hydrogen sulfide production from manure treated with metallic iron added as rods.

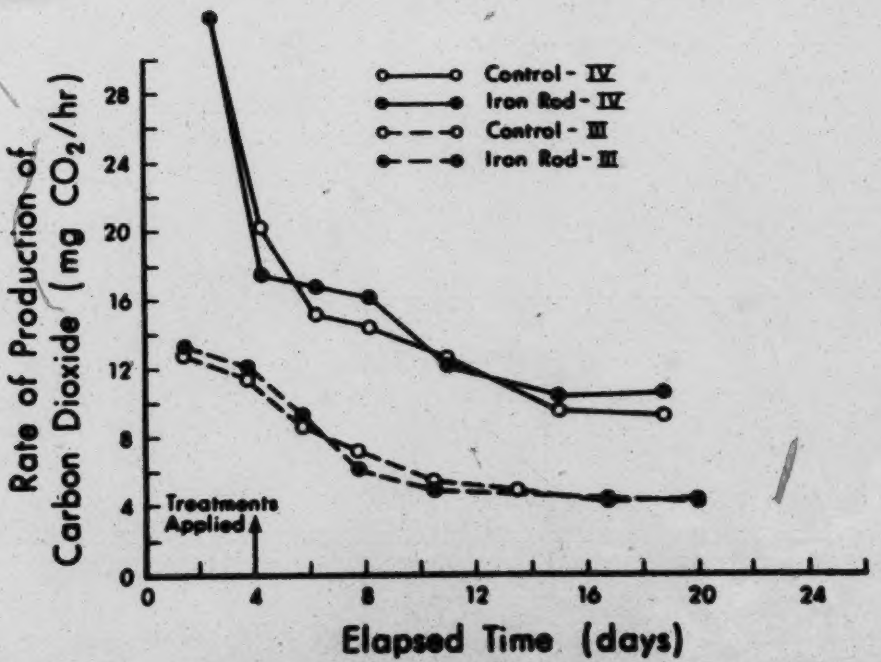

Figure 24b. Carbon dioxide production from manure treated with metallic iron added as rods.

With the exception of iron added in the ferric form, all iron additions resulted in an increase in the total sulfide content of the manure at the end of the incubation period compared to untreated controls. This suggests that sulfides may have been bound as insoluble iron sulfides and so were not released during the incubation period. Further evidence for precipitation of sulfides as iron sulfide was provided by the black color of all iron-treated manure.

Except in trials involving ferric iron, the total production of sulfides from iron-treated manure did not differ appreciably from the total sulfide production of the untreated controls. This observation suggests that addition of iron to the manure had little effect on the bacteria which produce the sulfides. Furthermore, the rates of carbon dioxide production from the iron-treated manure were very similar to those for the corresponding controls, further substantiating the claim that iron added either in metallic or ferrous forms did not adversely affect bacterial processes.

Addition of iron to manure in the ferric form resulted in lower amounts of total sulfides in the treated manure after digestion and apparently lower total sulfide production as compared to corresponding controls. Ferric iron is a relatively strong oxidizing agent and, when added to a highly reducing media such as anaerobic manure, will oxidize reduced inorganic compounds while being itself reduced to ferrous iron. In the presence of ferric iron, hydrogen sulfide in the media would very likely be oxidized to sulfate, and hence the reduced sulfide content of the treated manure. Because of the oxidizing effect of ferric ions added to manure, the values presented in Table 17 for total sulfide production from manure treated with ferric iron are only apparent. The total production in each case was no doubt much higher and quite probably similar to that of the untreated controls. Examination of Figure 22b suggests that the addition of ferric iron to manure caused a slight reduction in carbon dioxide production, and hence perhaps a decrease in bacterial action. The addition of ferric salts may have exerted a deleterious effect on bacterial activity by virtue of a decrease in the pH of the manure.

In the two trials with ferrous plus metallic iron, the objective was to add sufficient ferrous iron to precipitate sulfides already in the media. This was expected to increase the rate of corrosion of the metallic iron (14). In the case of ferrous iron plus iron powder (Trial I), enough ferrous iron was added to precipitate 100 mg of sulfide. The difference between the total sulfide contents of the manure in this treatment and in the corresponding control was approximately 90 mgs, suggesting that the entire effect on sulfide release could have been attributed to the ferrous iron alone. In the next trial with ferrous and metallic iron (Trial II), an iron rod was added instead of powdered iron, with only sufficient ferrous iron being added to precipitate 50 mg of sulfide. The difference between the total sulfide content of the treated manure and the untreated manure was approximately 70 mg in this case, so that 20 mg of sulfide may have been precipitated by iron released by corrosion of the iron rod. Comparing this 20 mg to the 17 and 13 mg difference between manure treated with iron rods alone and their corresponding controls, a greater rate of corrosion may indeed have occurred in the case of ferrous iron plus the iron rod than with the iron rods alone.

The results of the bench-scale trial with ferrous iron and with an iron pipe are presented in Table 21. The only parameter measured was the amount of sulfide released upon agitation of the digested manure. Clearly, the ferrous iron treatment quite effectively reduced the amount of sulfide released upon agitation as compared to the untreated control. However, addition of the iron pipe to the manure had no beneficial effect on sulfide release. Examination of the pipe revealed that the extent of corrosion was much greater than that which had been observed during the laboratory trials. The part of the pipe which had been in the bottom six to eight inches of the digestor was covered with black-flaky deposits, probably iron sulfide, which when scraped off revealed a shiny metal surface beneath. No corrosion had occurred further up from the lower end of the pipe, suggesting that activity of sulfate-reducing bacteria had been limited to that small region at the bottom of the digestor. Again, as in the laboratory trials, the rate of corrosion did not appear to be sufficiently great to effectively control sulfide evolution.

TABLE 21: RESULTS OF THE BENCH-SCALE TRIAL INVOLVING IRON TREATMENTS.

Digestor	Treatment	Sulfide released upon agitation (mg H_2S)
1	Ferrous iron	40
2	Control	3,640
3	Metallic iron	4,800

5.3.2 Liming.

When lime is added to manure, an increase in the pH of the manure is expected. As the pH is increased, proportionally less hydrogen sulfide gas will be released from the sulfide-containing solution. Extreme and/or shock increases in pH also may be toxic to bacteria, including those that produce sulfides.

Lime was added in these trials as calcium hydroxide. In the first liming trial, the pH of the manure 21 days after application of the lime at 1.5% by weight was 11.9. In the second trial, the rate of application of lime was reduced to 1.0% by weight. In this case, the pH of the manure 18 days after addition of the lime was 10.1.

Data collected in the ~~first~~ liming trial (Trial I) on the release of sulfides during incubation indicate that the rate of evolution of sulfides was much lower from the treated manure than from the untreated manure (Figure 25a). Similar data from the second trial (Trial II) appear not to be reliable. In this trial, the cumulative production of sulfides prior to the time of chemical additions was appreciably less for the manure that was later treated with lime than for the manure which was used as a control. Since no apparent reason can be suggested for this discrepancy, the data on sulfide release during incubation are not considered sufficiently reliable to interpret in detail.

In both liming trials, the release of sulfides upon agitation of the treated manure was eliminated, this in spite of the fact that the total sulfide content of the manure in each case was greater than that of corresponding controls. This result strongly suggests that, at a pH as high as 10.1, hydrogen sulfide is released only very

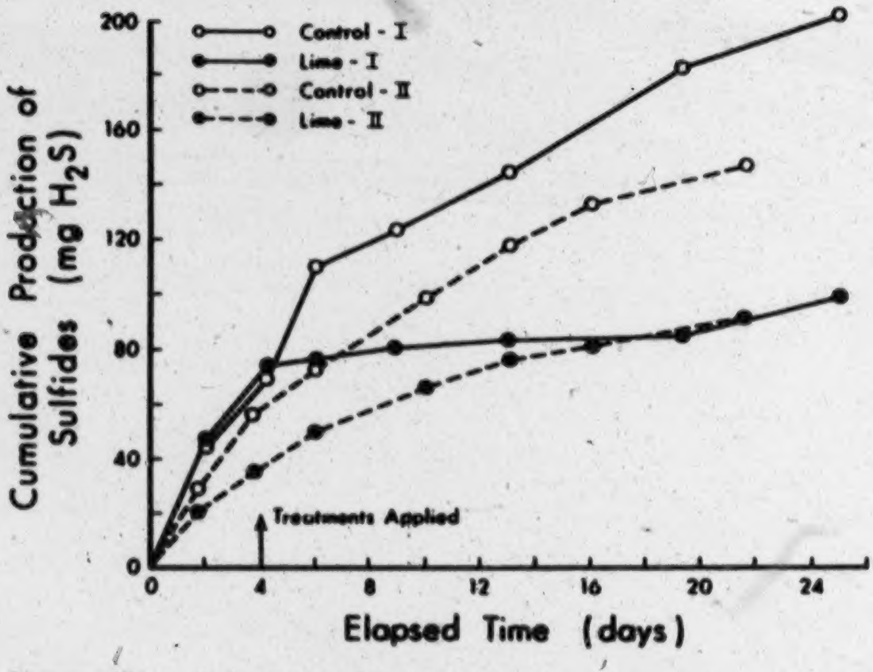

Figure 25a. Hydrogen sulfide production from manure treated with lime.

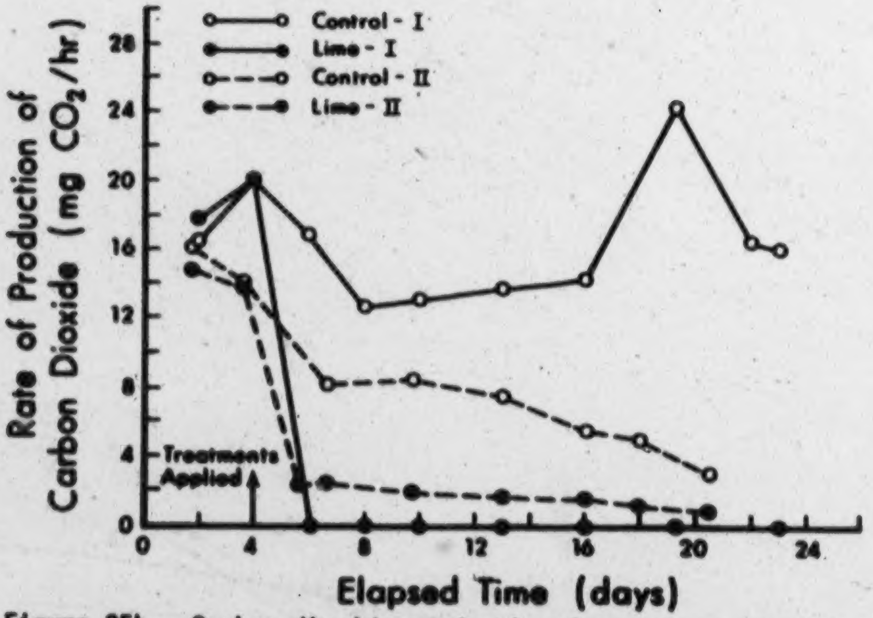

Figure 25b. Carbon dioxide production from manure treated with lime.

slowly, if at all, from a sulfide-containing manure solution.

In these liming trials, carbon dioxide production data may not be a reliable indicator of bacterial action in the treated manure. At high pH values, dissolved carbon dioxide exists only in very small amounts, the dissolved gas being converted to bicarbonate and carbonate in a fashion analagous to the soluble sulfide transformations explained in Section 2.3.1. Therefore, during the second trial, a small aliquot of the fermenting manure was assayed for sulfate-reducing bacteria. As indicated in Table 20, sulfate-reducing bacteria were absent and probably had been killed by the lime treatment. The corresponding control manure contained large numbers of sulfate-reducing bacteria, some of which were shown to be spore-forming species (31). Thus, even sporulating species of sulfate-reducing bacteria apparently were destroyed by liming. Although similar assays were not conducted during the first trial with lime, the same results probably would have been recorded since an even greater amount of lime had been added. In agreement with these findings, the total production of sulfides was substantially lower from lime-treated manure than from untreated manure.

Subsequent to the two liming trials reported above, another trial of an exploratory nature was conducted in an attempt to gain further insight into the effects of liming on sulfide production in, and release from, anaerobic manure. In this trial, the plastic digestors described in Section 4.1.1 were used.

The initial intent was to incubate samples of manure, limed to various pH values ranging from 6.5 to greater than 11, and to monitor the sulfide released upon agitation of each and the total sulfide composition of the contents of each digestor at the end of a 3-week incubation period. Theoretically, the data might have been expected to be similar to that shown in Figure 29. The amount of sulfide released upon agitation would be highest at the lowest pH and would decline with increasing pH until, at a pH greater than 9, none would be released. The total sulfide production, calculated as the sum of the sulfides released upon agitation and the sulfide content of the digested manure, would reach a peak somewhere between a pH of 7 and 8 (the pH corresponding to maximum activity of the sulfide-producing bacteria) and would decrease with increasing pH until a minimum level was reached at pH values somewhere around 10 or higher. The magnitude of this minimum level would correspond to the sulfide content of the manure prior to liming.

The results of the trial which was conducted are given in Table 22.

TABLE 22: RESULTS OF THE LIMING TRIAL USING THE PLASTIC LABORATORY DIGESTORS.

Lime Concentration (% by weight)	pH of manure at end of incubation	Sulfides released upon agitation (mg H_2S)
0.0	6.85	174
0.25	6.9	146
0.50	7.1	170
0.75	7.35	167
1.0	7.85	183
1.5	8.25	167

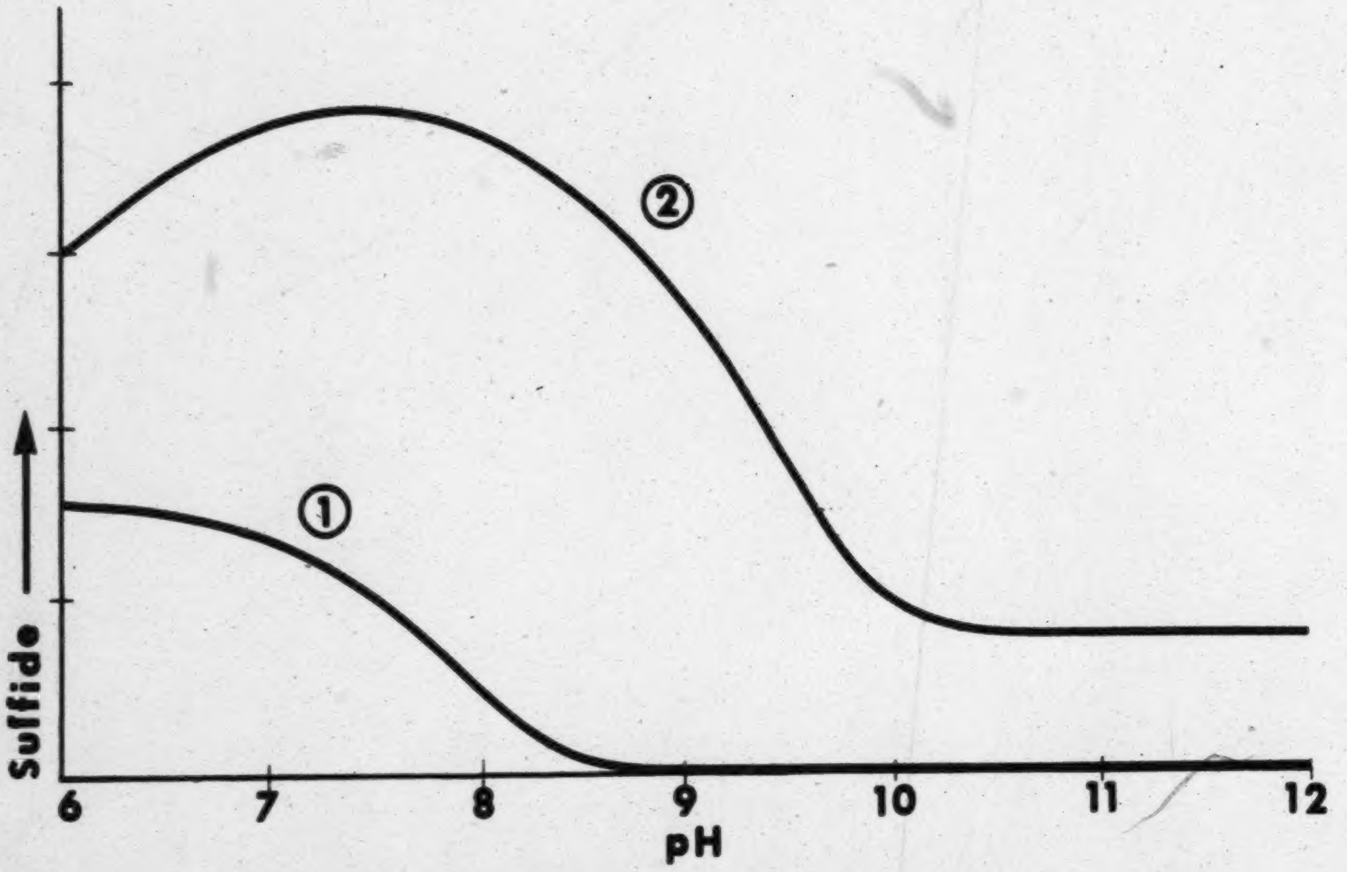

Figure 29. Theoretical relationship between the pH of manure and the evolution of sulfides: 1 - sulfides released upon agitation; 2 - total sulfides evolved.

Due to circumstances beyond the author's control, the length of the incubation period was extended to 30 days, instead of 21 as planned. At the end of 30 days, the amount of sulfides released upon agitation was approximately the same for all treatments. The highest pH measured at this time was 8.25, despite an earlier observation with similar manure (collected from the same installation) that the highest lime addition would increase the pH to greater than 11. These results suggest that the pH readings taken at the end of incubation were not the pH values that had existed earlier in the incubation period. A similar experience has been reported by Deibel (36) who found that regardless of the amount of lime added to poultry manure, after about a week's incubation the pH dropped rapidly to a range of 7 to 8. Surprisingly, other trials with lime, including those previously reported in this investigation, have not supported this phenomenon. Insufficient time was available during the investigation period reported herein to conduct further trials with lime, although the need for such trials is apparent.

5.3.3 Oxidizing Agents.

The results obtained with each of the oxidizing agents are sufficiently different to warrant a separate discussion of each.

5.3.3.1 Ammonium Persulfate.

Ammonium persulfate was applied in each trial at the rate of 1% by weight or, on an equivalent oxygen basis, at the rate of 2800 ppm O_2. At this rate, the chemical effectively prevented the evolution of hydrogen sulfide from the manure solution (Figure 26a). No hydrogen sulfide was released upon agitation of the digested

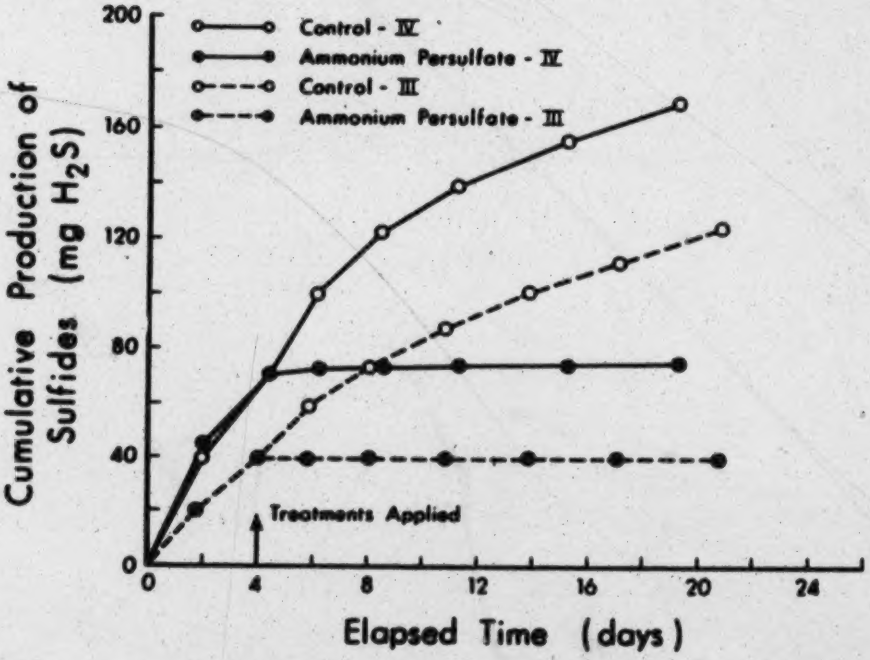

Figure 26a. Hydrogen sulfide production from manure treated with persulfate.

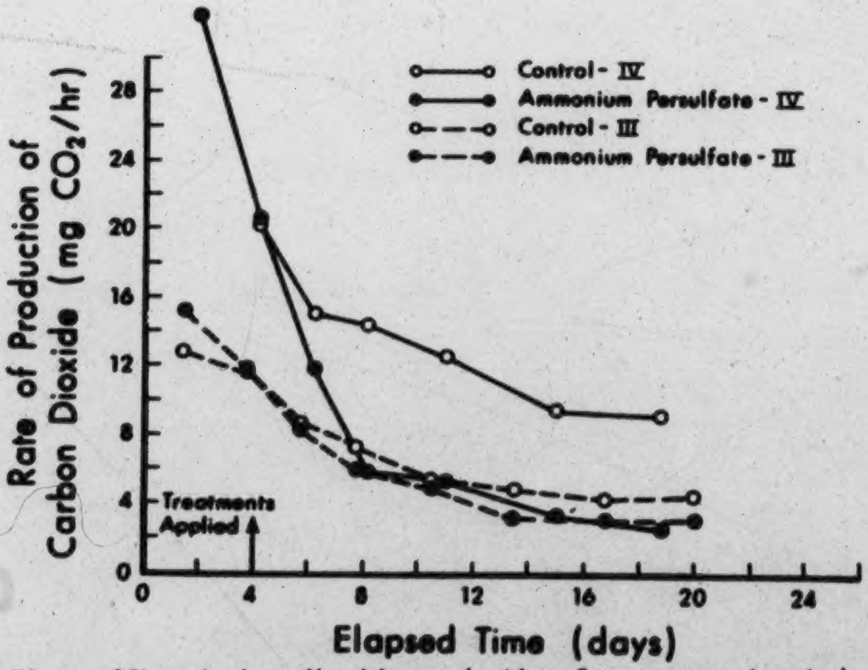

Figure 26b. Carbon dioxide production from manure treated with persulfate.

manure and essentially no sulfide remained in the digested manure (Table 17). Analysis of the manure for sulfate-reducing bacteria indicated that most of these bacteria had been killed by the chemical treatment (Table 20). The rates of carbon dioxide production from the treated manure were not substantially different than those from the corresponding controls, suggesting that some bacteria, supposedly aerobes and facultative anaerobes, had not been killed by the treatment. Thus, the primary effects of ammonium persulfate added to anaerobic manure would appear to be oxidation of sulfides existing in the manure and elimination of the activity of anaerobic sulfide-producing bacteria.

5.3.3.2 Potassium Permanganate.

In the first trial with potassium permanganate (Trial III), the chemical was added as a concentrated water solution. The rate of application was approximately 0.1% by weight or, on an equivalent oxygen basis, 200 ppm O_2. As shown in figure 27a, the evolution of sulfides was completely curtailed for the first two to four days after addition of the chemical; thereafter, there was a slow recovery back to normal sulfide evolution. The sulfate-reducing bacteria count approximately 10 days after chemical treatment did not differ greatly from that in the untreated manure. Carbon dioxide production during incubation of the treated manure paralleled that of the control manure. At the end of the incubation period, the total sulfide contents of the control and treated manure were essentially the same, as were the amounts of sulfide released upon agitation of the digested manure. The measured total sulfide production over the entire

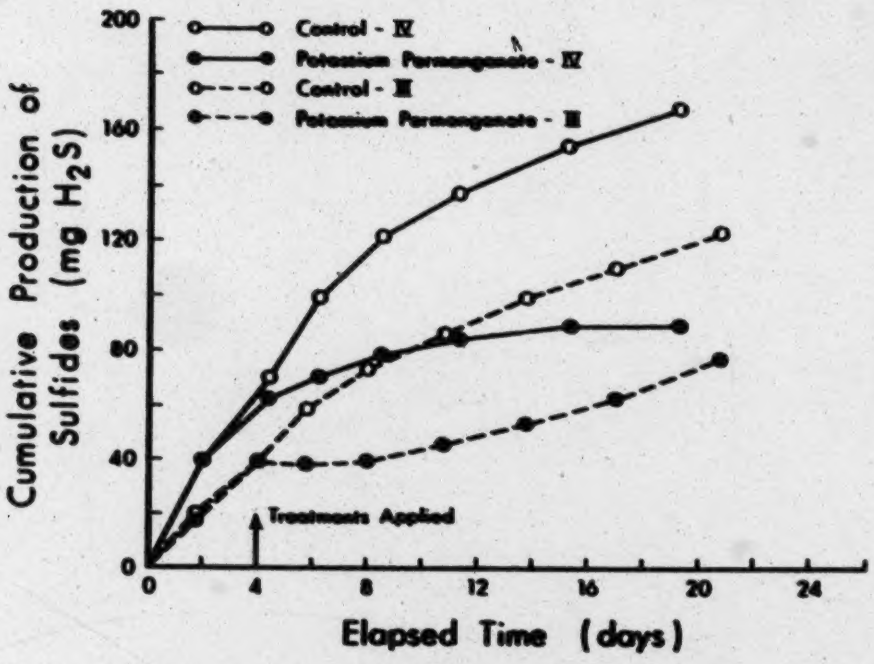

Figure 27a. Hydrogen sulfide production from manure treated with permanganate.

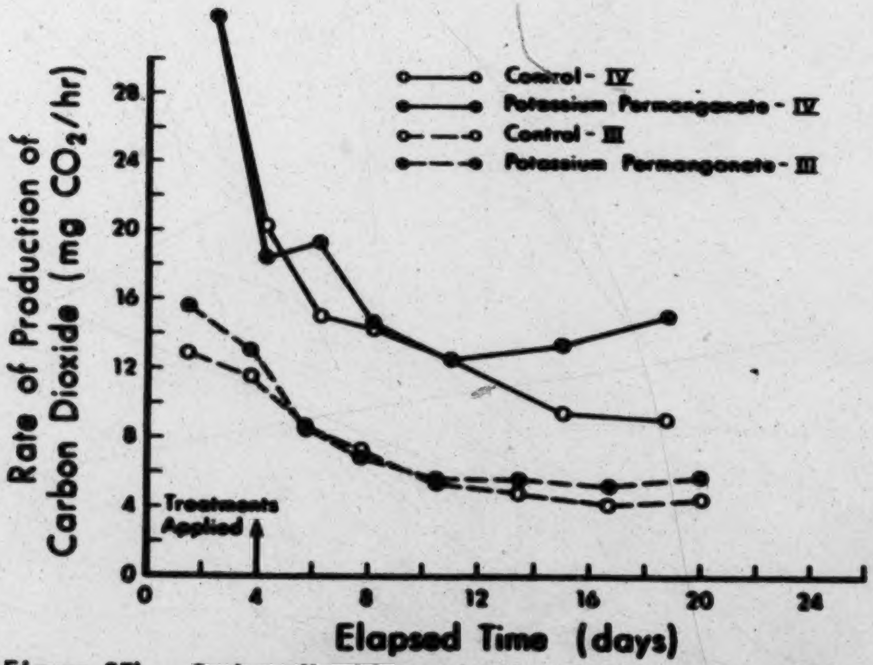

Figure 27b. Carbon dioxide production from manure treated with permanganate.

incubation period, however, was much less for the treated manure.

These results suggest that sulfides in the media were oxidized by the permanganate. After all of the permanganate had been reduced, sulfide production by the treated manure returned to the same rate as that by untreated manure. Unlike ammonium persulfate, potassium permanganate did not have a lethal effect on sulfate-reducing bacteria, although permanganate in fact may have retarded sulfide-production by these bacteria during the first few days after addition to the manure.

The results of the first trial with permanganate indicated that the treatment might have been more effective had more of the chemical been added. Therefore, in the second trial (Trial IV), the rate of application was increased to 0.25% by weight or, on an equivalent oxygen basis, 500 ppm O_2. However, to avoid excessive dilution of the treated manure, the permanganate had to be applied in solid form. As shown in Figure 27a, the rate of evolution of sulfides from the treated manure decreased relative to an untreated control after addition of the chemical, and continued to decrease even further during the remainder of the incubation period. Throughout the trial, spots of undissolved solid potassium permanganate could be seen throughout the manure. The total sulfide content of the digested chemically-treated manure was considerably less than that of the untreated manure and, consequently, less sulfide was released upon agitation. Furthermore, the total sulfide production during incubation of the treated manure was considerably less for the treated manure than that of the corresponding control.

These results indicate that the permanganate may have acted in a similar manner in both trials, except that in the second trial there was a continual slow release of oxidant into the manure solution throughout the incubation period. The reported ineffectiveness of potassium permanganate for controlling sulfide evolution from anaerobic manure during these trials appears to have been the result of insufficient rates of application in one case and inadequacy of mixing the chemical into the manure solution in the other.

5.3.3.3 Nitrate.

In the first trial with nitrate (Trial I), nitrate was applied as sodium nitrate at the rate of 0.5% by weight or, on an equal oxygen basis, at the rate of 1500 ppm O_2. As shown in Figure 28a, the rate of evolution of sulfides was depressed after chemical addition, but about 8 days afterwards returned to the same rate as observed for the control. During the period in which sulfide evolution was reduced, the color of the manure changed from a dark green to an amber color but, as sulfide evolution resumed, the color changed back to dark green.

In the second trial (Trial III), nitrate was added again as sodium nitrate, but on an equal oxygen basis with the ammonium persulfate treatments, or 2800 ppm O_2. In this trial, sulfide evolution from the treated manure was less than that from the untreated control throughout the entire incubation period. As in the first trial, the color of the manure changed to an amber color during the first part of the incubation period but, by about the 12th day of incubation, had changed back to the original dark green color. Unlike the first trial, the rate of carbon dioxide production from the nitrate-treated manure was higher than that from the control manure throughout the incubation and was much higher for a short

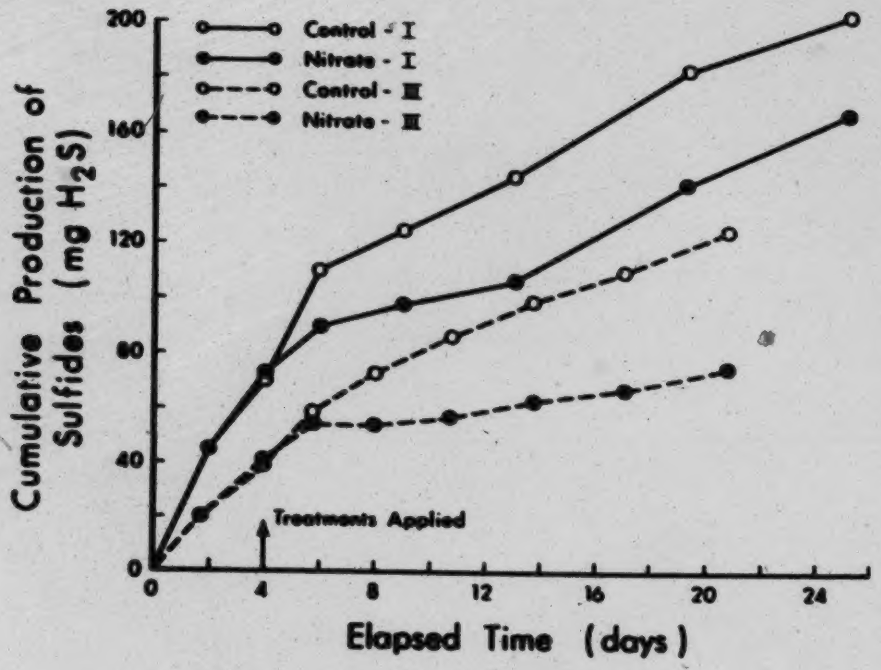

Figure 28a. Hydrogen sulfide production from manure treated with nitrate.

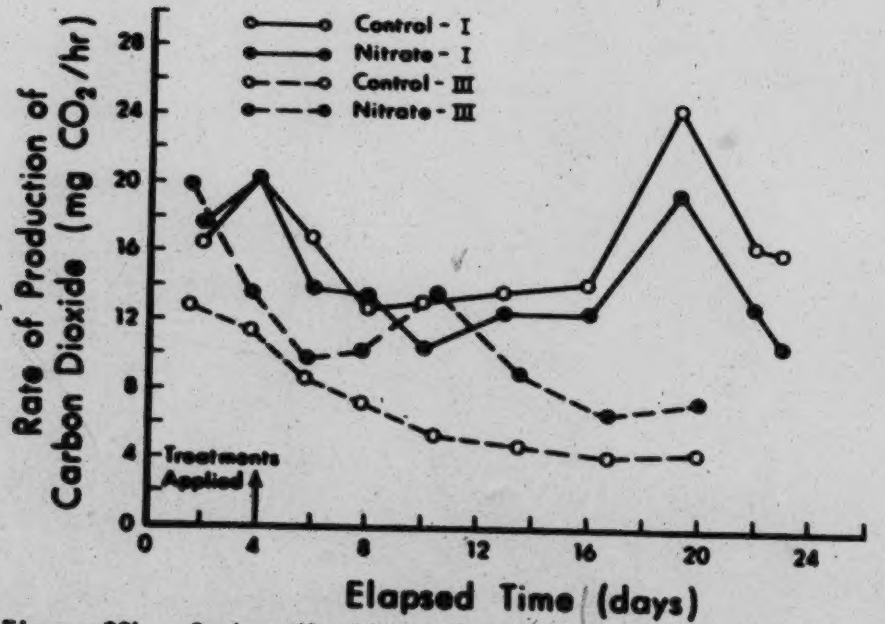

Figure 28b. Carbon dioxide production from manure treated with nitrate.

period beginning about 2 days after the chemical was added. During the time of high rates of carbon dioxide production, excessive bubbling and foaming were noted on the surface of the treated manure as compared to the untreated manure. Microbial examination of the manure after this time indicated that some sulfate-reducing bacteria had survived the nitrate treatment.

At the end of the first trial with nitrate, and just prior to the determination of the total sulfide content of the digested manure, the digestor holding the treated manure was broken accidentally; consequently, no further determinations could be made. In the second trial, a violent reaction occurred when acid was added to the digested nitrate-treated manure and some of the digestor contents foamed out over the top of the digestor. The analysis for total sulfides was continued, however, and the data for total sulfide content and total sulfide production are reported in this trial as minimum values (Table 17).

The results reported in Table 17 suggest that the sulfide content of the nitrate-treated manure was probably as great as that in the untreated manure. However, the amount of sulfides released upon agitation of the nitrate-treated manure were much less in both trials than the amounts released from the untreated manure, probably because of the much higher pH of the treated manure (Table 19).

The results of the two trials with nitrate indicate that the addition of nitrate to anaerobic manure delayed the evolution of sulfides. This delay in sulfide evolution may have been achieved through an alteration of the ORP of the manure. Nitrate did not appear to be capable of directly oxidizing sulfides, and was not lethal to all sulfide-producing bacteria.

5.3.4 Practical Implications.

5.3.4.1 Mixing.

To be effective, all chemicals must be mixed thoroughly into the manure that is to be treated. Mixing was not found to be a problem in the case of those chemicals which are very soluble in aqueous solution (e.g., sodium nitrate, ammonium persulfate, and ferrous chloride). However, the inability to achieve a uniform distribution in the manure of the chemical in the cases of lime, powdered iron, ferric salts, and potassium permanganate may have decreased the effectiveness of those chemicals. This requirement for large amounts of mixing may limit seriously the practicality of using the latter group of chemicals. Complete mixing is difficult to attain, and may result in an increased evolution of noxious and malodorous gases.

If powdered iron were added on a field-scale basis, some attempt would probably need to be made to add the powder in such a way that an excess of iron was maintained yet, upon emptying of pits, for example, the unused powder could be reclaimed.

5.3.4.2 Safety.

All chemicals with the possible exceptions of nitrate, permanganate and persulfate are apparently safe to use. In the case of the oxidizing agents, there is a possibility that toxic concentrations of poisonous gases could arise as a result of the reduction of large amounts of the chemicals under special conditions. Both potassium permanganate and ammonium persulfate are very strong oxidizing agents and, in the solid form, accidentally could cause severe "burns" to the skin of both animals and operators. However, because persulfate most probably would be applied as a dilute water solution, the possibility of its causing such damage would be minimal.

5.3.4.3 Byproducts.

The byproducts formed as a result of iron treatment are iron sulfides. Sometimes termed "iron pyrites", ferrous sulfides have been used as sulfur fertilizer (7) so would not be expected to be harmful to soil if treated manure were spread on cropland. In the case of iron being added to manure either as ferrous or ferric chlorides, however, the treated manure could prove harmful to plant growth if it were field spread due to the large concentration of chloride salts. Perhaps some difficulty could be experienced with an accumulation of iron sulfides in the bottom of manure storage facilities; however, both laboratory and bench-scale trials indicated that the iron sulfide precipitate remained suspended throughout the manure solids, rather than settling to the bottom.

Both sodium nitrate and ammonium persulfate (110) could be used as fertilizers; hence a slight excess in the addition of such chemicals to manure would not likely result in undesireable effects should the treated manure be field-spread. However, ammonium persulfate, like potassium permanganate, is a strong oxidizing agent. If applied to manure in large excess, the treated manure perhaps could have a sterilizing effect on soil microorganisms. Such large excesses are not likely to occur for obvious economic reasons. Furthermore, in the case of sodium nitrate, excessive amounts of sodium in the treated manure (lime added as calcium hydroxide) from pits or other storage facilities would not appear to be a problem, based on experience gained during this investigation. If spread on cropland, lime-treated manure probably would cause an increase in soil pH, the magnitude of this increase dependent upon the quantity of manure applied and the buffering capacity of the soil. Such an increase in pH might either be beneficial or detrimental to crop production, depending on the initial pH of the soil and the specific crops being grown. In any case, the increase in soil pH which might be expected following reasonable applications of lime-treated manure have been computed to be quite small (128).

5.3.4.4 Odor Reduction.

No attempt was made during this investigation to systematically evaluate the effect of the various chemical treatments on the odor offensiveness of the treated manure. However, notes were made during the four incubation trials of significant differences in odor quality between treated and untreated manure.

Iron treatments, compared to controls, did not appear to reduce the offensiveness of the manure odor; however, no evaluation was made of odors during the period of agitation when the odors from the treated manure probably would have been less offensive than from untreated manure because of the reduced concentrations of hydrogen sulfide.

Unlike the iron treatments, the application of oxidants and of lime noticeably changed the quality of the odors from the manure as compared to controls. In the cases of lime and nitrate treatments, the characteristic manure odor was masked largely by a strong ammonia odor. The odor from manure treated with either permanganate or persulfate was judged by the author to be much less offensive than that from either untreated manure or manure treated with any of the other chemicals.

5.3.4.5 Specific Applications and Economics.

This investigation has shown that the evolution of sulfides from anaerobically fermenting manure is reduced by the addition of ionic or metallic iron to the manure during fermentation. Iron, added as ferrous salts or as a fine powder of metallic iron, effectively prevented the accumulation of soluble sulfides and gaseous hydrogen sulfide without adversely affecting the bacteria involved in the anaerobic digestion process. Treatment of manure with iron in these forms would appear to be especially useful in cases where waste liquefication and organics reduction are desired, such as in anaerobic methane digestion. By precipitating sulfides as insoluble iron sulfides, iron additions to manure in anaerobic digestors could minimize the problems of sulfide toxicity (as explained in Section 2.3.3) and of hydrogen sulfide in the gases collected from the digestors. A toxicity problem could result from repeated applications of ferrous salts if the anions released were toxic to bacteria. This possibility of toxicity is eliminated in the case of iron added in the metallic form and, as such, powdered metallic iron appears to be the best overall alternative for sulfide control during anaerobic digestion. Information concerning the cost of powdering iron for this application could not be located by the author.

The other chemicals evaluated in this investigation could be useful for controlling hydrogen sulfide evolution from anaerobically stored manure in cases where waste stabilization during storage is not of primary importance. Alternatively, they could be added to manure just prior to removal from storage and disposal by field spreading. In addition to controlling hydrogen sulfide, persulfate and permanganate may effectively control most other malodorous emissions from anaerobically stored manure as well. Treatment of manure with ammonium persulfate, in particular, would appear to be especially advantageous in the case of anaerobic lagoons. Since the worst odor problems occur during the time of emptying anaerobic lagoons and during subsequent field spreading operations, ammonium persulfate could be applied to the surface of the lagoon just prior to agitation of the lagoon contents. In such an application, the minimum effective application rate of the chemical would likely be much less than that used in this investigation, since only short-term control would be necessary.

The costs of chemically treating manure for odor control are difficult to estimate. In the first place, accurate figures for the costs of the various chemicals are difficult to acquire. For example, the cost of lime (as calcium oxide) from laboratory supply companies is listed at $0.25/lb or more, whereas the Edmonton Domestic Water Treatment Plant (42) buys calcium oxide for approximately $22.50/ton, depending on the purity of the chemical. The respective minimum costs of sodium nitrate, potassium permanganate and ammonium persulfate from the same laboratory chemical supply companies are $0.68/lb, $0.95/lb, and $0.79/lb. Assuming that these chemicals could be supplied in bulk at savings comparable to that indicated for lime, the cost of each would be reduced to $61.20/ton, $95.50/ton, and $71.10/ton, respectively.

Further to the problem of estimating the costs of chemicals, information is lacking on the optimum application rates of the chemicals for use under practical field-scale conditions. The minimum application rates of lime (as calcium hydroxide), sodium nitrate and potassium permanganate shown to be effective in laboratory trials were, on a weight basis, 1.0%, 0.5% and 0.25%, respectively. These application rates are probably close to the minimum rates that might be expected to be effective under field conditions. However, as previously noted, ammonium persulfate probably would be effective for short-term odor control at rates considerably lower than that used in these laboratory trials. Assuming that persulfate would be two-thirds as effective as permanganate if each were applied at the same molar concentration[a], the minimum effective concentration of ammonium persulfate could be as low as 0.5% by weight. All of these rates are applicable in the case of swine manure with a total solids content of approximately 5%.

Using the figures presented above for the minimum effective application rates for short-term odor control, and the calculated discount prices for each chemical, swine manure could be treated with lime, sodium nitrate, potassium permanganate and ammonium persulfate. for as little as $0.84, $0.76, $0.53, and $0.90 per hog marketed, respectively. These costs are based on a lifetime production of manure by feeder pigs equal to 5000 lb.[b]

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[a] Reduction of one mole of permanganate under alkaline conditions involves the transfer of three electrons, compared to two electrons transferred by the reduction of one mole of persulfate.

[b] Weekly production of manure with a moisture content of 95% is approximately 3.75 cu. ft/hog. Multiplied by 22 weeks, the lifetime production would be 82.5 cu. ft or 5190 lb. These figures are calculated from data given in the Canada Animal Waste Management Guide (24).

Clearly, these estimates are only approximate, and are based on a large amount of speculation regarding effective application rates and bulk chemical prices. However, they may serve to indicate the relative economics of chemical treatment and aeration for odor control. One of the lowest reported costs of aerating hog wastes is $0.25/hog marketed (132); however, usually much higher estimates are given. Furthermore, in the case cited, the operating cost was based on an electrical cost of 1.[illegible] cent per Kw-hr, a figure which could increase several fold in the near future as a result of impending world energy shortages. Thus, after an accounting is made for the extra capital costs associated with aeration, chemical treatment of manure may be an 'economical'alternative to aeration as a solution to the manure odor and toxic gas problem.

5.4 Experimental Limitations.

5.4.1 Manure Sampling.

The manure samples obtained from all three commercial swine operations were judged to be closely representative of the larger bodies of manure from which they were collected. However, none of the sampling methods were capable of providing totally undisturbed, unaerated samples for analyses. Thus, the values obtained for the total sulfur composition of the samples, especially those from Installation A, would not account for hydrogen sulfide evolved from the samples during their collection and handling prior to analyses. Similarly, pH values of the samples must not be considered entirely reliable since a loss of volatile constituents from the manure during sampling could cause changes in pH.

5.4.2 Chemical Analyses.

The following limitations may be noted regarding the analytical procedures employed in this investigation:

(a) Homogenization of manure samples was considered necessary to increase the chances of securing small representative subsamples of the manure for chemical analyses. However, in this investigation, representative subsamples apparently were not obtained from liquid swine manure samples, even after blending at high speed with a Waring commercial blendor. Despite its ineffectiveness, blending of the samples resulted in excessive amounts of entrapped air and large changes in the properties of the samples, including changes in the concentrations of volatile dissolved gases and substantial pH increases.

(b) The method employed for determination of water-soluble sulfate-sulfur in liquid manure samples was totally unreliable. The method apparently did not distinguish between water-soluble sulfate and other easily reducible sulfur compounds; neither did the method of extraction guarantee that a representative amount of reducible sulfur would be contained in the filtrate used for analysis. The value obtained and recorded for each sample as water-soluble sulfate, then, was actually some unknown compromise between total sulfate-sulfur and water-soluble sulfate-sulfur.

(c) The methods employed for determination of total sulfur in liquid manure and fresh excreta samples, and for determination of total-sulfate-sulfur in fresh excreta samples were apparently reliable, providing representative subsamples for analyses were extracted from the larger bulk samples. In the case of urine and feces samples, subsampling was not a problem, but in the case of the slurried manure samples, subsampling did limit severely the accuracy of the sulfur determinations. Furthermore, whereas in the case of fresh excreta samples the total sulfur could be assumed to be the sum of total sulfate-sulfur and organic-sulfur, some sulfides also may have been included in the measured sulfur compositions of manure and wastewater samples. Consequently, comparisons between the total sulfur compositions of manure samples collected from the various installations may be suspect since different amounts of sulfides may have been lost from the samples during collection. For example, the organic plus total-sulfate sulfur compositions of samples from Installations B and C were quite likely the same, or at least nearly the same, as the measured value for the total sulfur composition of those samples. However, in the case of samples from Installation A, the recorded values for total sulfur no doubt included significant amounts of sulfides.

5.4.3 Gas Analysis.

The methods of gas analysis employed during the laboratory and bench-scale trials with the various chemical treatments were subject to the following limitations:

(a) During incubation of manure samples in the laboratory, carrier gas was swept continuously through the digestors, thereby keeping the partial pressure of all gases except nitrogen and carbon dioxide approximately equal to zero. By this method, the amount of sulfide which was collected in each gas scrubber could be considered an indication of the relative rate at which the concentration of dissolved hydrogen sulfide was changing in each of the manure samples. This relationship between sulfide production in the manure and sulfide collected in the scrubbers was dependent upon the following assumptions:

(i) the initial concentration of dissolved hydrogen sulfide was the same in all samples of manure (chemicals were not added to the manure until the fourth day of incubation to check this assumption)

(ii) the temperature of each sample was the same (assumed to be true since all samples were incubated at the same time in the same environmentally-controlled chamber).

Thus, any differences in the amounts of sulfides collected from each sample were considered indicative of differences in the rate of evolution of sulfides from each of the samples. However, more information was needed to differentiate between the following possible specific effects of each treatment on sulfide evolution:

(i) changes in the rate of production of sulfides,

(ii) removal of soluble sulfides from solution, such as by precipitation,

(iii) changes in the pH of the sample and thus the equilibrium between gaseous and dissolved hydrogen sulfide, and

(iv) changes in surface conditions of the samples and thus the rate of sulfide desorption.

In addition to the above-mentioned procedures, a better sulfide monitoring program could involve continuous monitoring of pH and total soluble sulfides, and more frequent microbial analyses, including total bacterial counts and counts of specific groups of sulfide-producing bacteria.

(b) Under actual storage conditions in the field, the removal of gases from the atmosphere immediate to the manure will not always be as complete as experienced during the laboratory incubation trials. Hence, the measured rates of evolution of sulfides are probably higher than those that would occur under field conditions.

(c) In the laboratory trials, chemicals were mixed vigorously into the manure samples by swirling the digestors. This agitation of the manure no doubt caused an increase in the evolution of sulfides that would have been recorded together with sulfides actually produced during the first collection period after chemical additions. Thus, data on the rate of sulfide evolution shortly after the application of chemical treatments are not accurate on an absolute basis; however, relative to the controls that had been agitated as well, the cumulative sulfide production data probably would not have been much different had this source of error not existed.

(d) Determination of the amount of sulfides released upon agitation of manure samples in both laboratory and bench-scale trials involved purging the samples with carrier gas. The rate of purging could perhaps have influenced the rate of diffusion of dissolved hydrogen sulfide from the manure solution. Since no flow meters were used, the rate of gas flow during purging was regulated only by flow-control valves and was measured by the rate of flow of gas bubbles through the scrubbers. In the case of the laboratory trials, this method appeared to allow fairly good control, and the data collected may be assumed to be fairly reliable. However, in the case of the bench-scale trial, a parallel arrangement of five scrubbers was utilized and the rate of gas flow through the scrubbers was such that individual bubbles did not form, making it extremely difficult to set the flow of gas during agitation of each digestor at exactly the same rate. Thus, flow meters should be used in any future trials involving a similar method for determination of sulfides released upon agitation of digested manure.

(e) Attempts to use wet chemical techniques for gas analysis in the bench-scale trial were quite unsuccessful, due to the very large amounts of gas that were evolved. Chromatographic analyses no doubt would be much better when larger amounts of manure are involved.

(f) During this investigation, no distinction was made between various forms of sulfides evolved from manure. For example, carbonyl sulfide and hydrogen sulfide would likely both be trapped in the cadmium acetate absorbent solution. This limitation was not considered serious, but an attempt could be made in any further trials of a similar nature to separate the various forms of sulfide by selective absorption in appropriate solutions, or by chromatographic analyses. The major limitation to chromatographic analyses would appear to be the requirement to concentrate the gases to enable detection by currently available methods (59).

5.4.4 Digestor design.

The conical shaped glass digestors employed in the laboratory incubation trials with the various chemical treatments lacked the following desireable features:

(a) provision for occasional or continuous mechanical mixing of the digestor contents.

(b) ports for sampling the digestor contents at various locations throughout the digestor. (In this investigation, the tops were removed from the digestors and samples were removed by pipetting from specified depths).

(c) provision for constant monitoring of the pH of the manure during incubation.

(d) longer necks on the tops of the digestors to prevent foam produced during mixing, especially after acid treatment, from exiting via the gas outlet ports.

6. SUMMARY AND CONCLUSIONS

A summary of results obtained in this investigation, and the conclusions drawn, are as follows:

(1) Sulfur was excreted largely as organically-bound sulfur in the feces and as sulfate-sulfur in the urine of feeder pigs.

(2) The partition of total sulfur excretion between the feces and urine, and the total amount of sulfur excreted by feeder pigs, were dependent upon the nature of the diet. The amount of sulfur excreted in the feces, expressed as a percentage of the total sulfur intake in the feed eaten, was nearly constant, whereas the amount of urinary sulfur excretion, expressed in the same manner, was extremely variable.

(3) On average, the feeder pigs from which excreta were collected retained about 29% of their total sulfur intake and about 44% of their total nitrogen intake. These differences in nitrogen and sulfur retention were reflected in generally lower nitrogen:sulfur ratios for the excreta samples than for the feed eaten.

(4) On the basis of the relative availability of the substrate, dissimilatory sulfate reduction probably would be the primary source of sulfides from anaerobic decomposition of the fresh excreta samples.

(5) Data collected in this investigation on the sulfur content of manure are too unreliable to interpret in detail. The total sulfur content of liquid swine manure samples varied from 0.34% to 1.36% on a dry matter basis, and from 116 ppm to

385 ppm on a wet basis. The nitrogen:sulfur ratio of the same samples varied from 6.83 to 15.82. Differences were noted in the nitrogen:sulfur ratios of manure collected from different swine production facilities. Such differences could be accounted for by differences in the classes of swine being fed, and in manure management, at the different installations.

(6) The results of laboratory and bench-scale trials involving the addition of ferrous salts to anaerobic swine manure indicate that, if large doses of the iron could be economically attained, the evolution of sulfides from manure could be virtually eliminated. Ferrous iron exerts its effect on the evolution of sulfides by precipitating soluble sulfides as iron sulfide.

(7) Ferric iron was not shown to be especially effective in reducing the evolution of sulfides from anaerobic swine manure in laboratory-scale incubation trials. This apparent ineffectiveness may have been the result of excessive applications of ferric salts, causing a decrease in the pH of the treated manure and, consequently, an increase in the rate of desorption of sulfides from the manure. Ferric iron not only precipitates sulfides as iron sulfide, but also oxidizes reduced sulfur compounds in the manure.

(8) Powdered iron was almost as effective as ferrous iron in reducing the evolution of sulfides from anaerobic swine manure during laboratory incubation trials; however, metallic iron added to manure as rods or pipes was not shown to be effective in either laboratory or bench-scale trials, although severe

corrosion of the metal did occur. Metallic iron exerts its effect on the evolution of sulfides from manure by precipitating soluble sulfides as insoluble iron sulfide.

(9) Liming manure to maintain a pH greater than 10 was shown to be relatively effective in controlling the evolution of sulfides from anaerobic swine manure during laboratory-scale incubation trials. Liming to a pH of nearly 12 was shown to be even more effective; however, under field conditions, the advantages of the higher rate of application of lime likely would not be as evident. These applications of lime apparently were lethal to sulfate-reducing bacteria which could account for the reduced production of sulfides from the treated manure. Liming also reduced the rate of desorption of dissolved hydrogen sulfide from the manure solution.

(10) Nitrate, added to anaerobic swine manure in laboratory trials at the rate of 750 ppm as NO_3-N effectively delayed the production of sulfides from the manure for up to eight days. Added as NO_3-N at the rate of 1400 ppm, sulfide production was delayed for over two weeks. The presence of nitrate in anaerobic manure apparently retards the activity of the bacteria that produce sulfides.

(10) Addition of ammonium persulfate to anaerobic swine manure at the rate of 1.0% by weight as $(NH_4)_2S_2O_8$ was shown to effectively eliminate the evolution of sulfides from the manure during laboratory incubation periods. Added at this rate, soluble sulfides in the manure were oxidized and most

sulfate-reducing bacteria apparently were killed by the chemical treatment.

(12) Potassium permanganate, added to anaerobic swine manure as a saturated water solution at the rate of about 0.1% by weight $KMnO_4$ eliminated the evolution of sulfides for about four days during laboratory-scale incubation trials. Added as solid $KMnO_4$ at the rate of 0.25% by weight, potassium permanganate reduced but did not eliminate the evolution of sulfides from anaerobic swine manure. At the rates applied, the chemical apparently oxidized soluble sulfides and retarded the activity of the bacteria which produce sulfides.

(13) Although no systematic evaluations were made of the effects of each chemical treatment on the overall odor of the treated manure, odor from the manure treated with either permanganate or persulfate did not appear to be as offensive as the odors from untreated manure or manure treated with any of the other chemicals.

(14) With the possible exception of permanganate, all of the chemicals are apparently safe and convenient to use. Potassium permanganate handled as a solid could cause accidental burns to the skin of animals and operators.

(15) Of the chemicals evaluated in this investigation, either persulfate or permanganate appear to offer the best solution to the problem of sulfide evolution from anaerobic swine manure, and perhaps to the problem of manure odors in general. Either ferrous or powdered iron would be most suitable for control of sulfide evolution

and of the concentration of soluble sulfides in cases where alteration of the bacterial population is undesireable.

(16) The relative effectiveness of each of the various chemicals for controlling the evolution of hydrogen sulfide from anaerobic swine manure has been demonstrated in batch incubation trials. Before any of the chemicals can be recommended for application under field conditions, however, further testing in pilot-scale continuous-flow trials is necessary.

7. SUGGESTIONS FOR FURTHER STUDY

The experience gained in this investigation would suggest the need for further study in the following subject areas:

(1) Several chemicals have been shown to effectively reduce the evolution of sulfides from anaerobic swine manure in laboratory and bench-scale incubation trials. Their effectiveness should be demonstrated in pilot-scale trials before a final evaluation of their efficacy is undertaken. A more detailed economic analysis also is required to evaluate the practicality of chemical control of sulfides.

(2) Some of the chemicals shown to effectively minimize the evolution of sulfides from anaerobic manure also may have reduced the evolution of other noxious and malodorous gases. Future trials of the type conducted during this investigation should include odor evaluations in addition to measurements of gas production.

(3) Each of the chemicals used in this investigation may have been more effective at either lesser or greater concentrations. A series of laboratory-scale trials should be conducted to determine the optimum rates of application of each chemical using different manure samples and under different environmental conditions.

(4) Metallic iron added to manure as a finely ground powder has been shown to effectively prevent the evolution of sulfides from anaerobic manure, whereas metallic iron added as rods or pipes was generally ineffective. Trials should be conducted to determine the optimum size of metallic iron particles for

effective prevention of sulfide evolution. Other metals, such as the zinc in tin cans, also could be evaluated for their usefulness in preventing sulfide evolution from anaerobic manure.

(5) The effectiveness of metallic iron in preventing the evolution of sulfides from anaerobic manure is dependent upon corrosion of the metal. This corrosion process is hastened by the activity of sulfate-reducing bacteria in the manure. Whereas optimum activity of these bacteria occurs in the pH range of 7 to 8, the pH of iron-treated manure in this investigation was less than 7. Trials could be conducted to evaluate the effect of a combined chemical treatment of manure involving liming to pH of 8 and addition of metallic iron.

(6) A technique known as cathodic protection has been employed numerous times in the past to prevent corrosion of buried metal pipes.

According to Booth (14),

> "In this method of protection the entire structure to be protected is made into the cathode of an electrolytic cell either by connecting to it remotely situated bars of a more electronegative metal (acting as anodes) or by imposing a direct current between the structure and remotely situated and expendable anodes to which the corrosion is transferred..."

In the present application, the reverse of cathodic protection might be used to "cause" a large piece of iron or scrap metal to corrode. The technical and economic feasibility of this approach could be investigated in laboratory trials.

(7) The effectiveness of chemical oxidants for control of hydrogen sulfide evolution from aqueous solutions is dependent upon the pH of the media. Both permanganate and nitrate probably would be more effective under acidic or neutral conditions than under alkaline conditions such as were experienced in this project. Trials could be conducted, therefore, to evaluate the effect of a combined treatment of manure involving lowering of the pH of the media and the application of chemical oxidizing agents.

(8) Odors are produced in manure by a host of micro-organisms, the identity of which are not generally known. Research should be conducted to enumerate, isolate and identify the bacteria associated with the production of odorous compounds from manure, and to evaluate the ecological significance of each of the major groups so identified.

(9) Since the production of odors from manure is almost totally the result of bacterial activity, further work involving the identification and control of odors associated with manure must have the close cooperation of a microbiologist. Furthermore, because the compounds that probably are causing odors are often complicated with respect to their identification, quantification, and possible reactions, the cooperation of an organic chemist is required for effective odor control research.

(10) The wide variations in results obtained upon analysis of multiple subsamples of the same manure sample clearly indicate the need for superior techniques than high-speed blending to obtain

homogeneous samples for subsampling, and techniques of analyses designed specifically for animal wastes.

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APPENDIX A: NOMENCLATURE AND MORPHOLOGY OF SULFATE-REDUCING BACTERIA.

A summary of the nomenclature and morphology of sulfate-reducing bacteria is given on the following pages. The information presented is taken from reviews by Campbell and Postgate (23) and Postgate and Campbell (168).

Desulfovibrio	Desulfotomaculum
non-sporulating	spore-forming
Gram-negative vibrios (sometimes sigmoid or spirilloid and occasionally straight)	Gram-negative straight or curved chains
obligate anaerobes	obligate anaerobes
polar flagellated	peritrichously flagellated
mesophillic (sometimes halophilic)	mesophilic or thermophilic
contain cytochrome C_3 and desulfoviridin	terminal or subterminal sporulation
some degree of antigenic cross reaction	show cross antigenicity
hydrogenase usually present	
facultative or obligate sulfate-reducers	
pathogenicity not recorded	
habitat: sea water, marine mud, fresh water and soil	habitat: fresh water, soils, geothermal regions, spoiled foods, insect intestines, and rumen contents

D. desulfuricans (type, species)	D. nigrificans (Formerly Clostridium nigrificans)
vibrio, 3-5 by 0.4-1μ	rods, 0.3-0.5 by 3-6μ
monotrichous	rounded ends
obligate anaerobe (E_h<-100m.v.)	sometimes paired
Temperature range: 28-44°C	habitat: compost heaps, thermal spring waters, "sulfur-stinker" spoilage of foods

APPENDIX A: Continued

Desulfovibrio	Desulfotomaculum
D. *vulgaris* as for D. *desulfuricans* except for some nutritional differences	D. *ruminis* (formerly "Coleman's organisms") rods, 0.3 by 3-6μ rounded ends sometimes paired habitat: rumen contents of sheep
D. *salexigins* as for D. *desulfuricans* except for some nutritional differences; also halophilic	D. *orientis* (formerly *Desulfovibrio orientis*) rods, 1.5 by 5μ fat, curved rods sometimes paired habitat: soil
D. *gigas* curved rods, 5-10 by 12.-1.5μ often in chains lophotrichous E_h = 80 m.v. at pH = 7	
D. *africans* long, sigmoid rods, 5-10 by 0.5μ lophotrichous haloduric	

APPENDIX B: RATIONS FED AT INSTALLATIONS FROM WHICH MANURE SAMPLES WERE COLLECTED FOR INCUBATION TRIALS.

(1) Installation A

Class of Swine	Protein Content of Ration	Constituents of ration (% of total)				
		Barley	Wheat	Soybean Supplements A	Soybean Supplements B	Fish Meal
sows	15.0	80	-	-	20	-
weaner pigs	18.0	-	78.3	14.7	-	7
grower-finisher pigs	14.5	86.7	-	13.3	-	-

Composition of soybean supplements (lb/ton of supplement)

Constituent	A	B
soybean meal	1570	1120
dehydrated alfalfa meal	0	500
salt	50	50
ground limestone	135	100
dicalcium phosphate	150	175
copper sulfate	10	0
vitamin premix	75	50
trace mineral premix	7.5	5
antibiotic	2.5	0
	2000	2000

(2) Installation C

Ration for grower-finisher pigs consisted of ground barley (86%) plus a commercial swine grower supplement (14%). Information on the composition of the commercial supplement was unavailable.

APPENDIX C: DIETS FED TO FEEDER PIGS DURING METABOLISM TRIALS.

	Treatment							
Ingredient	1	2	3	4	5	6	7	8
Barley	400	400	400	400	400	400	400	400
Wheat	405	331	321	326	331	321	326	395
Stabilized tallow	30	10	10	10	10	10	10	30
Soybean meal	102	96	96	96	96	96	96	102
Fishmeal	20	20	20	20	20	20	20	20
Iodized salt	5	5	5	5	5	5	5	5
Ground limestone	8	8	8	8	8	8	8	8
Calcium phosphate	20	20	20	20	20	20	20	20
Mineral-vitamin premix	10	10	10	10	10	10	10	10
Rapeseed (Span)	0	100	100	100	0	0	0	0
Rapeseed (Zephyr)	0	0	0	0	100	100	100	0
Chemstor	0	0	10	5	0	10	5	10
	1000	1000	1000	1000	1000	1000	1000	1000

APPENDIX D: ABSORBENT SOLUTIONS USED TO COLLECT AND CONCENTRATE HYDROGEN SULFIDE AND CARBON DIOXIDE.

1) **Cadmium acetate solution** -

(absorbs sulfides and traps them as insoluble CdS)

61 gm Cadmium acetate ($Cd(CH_3COO)_2.2H_2O$)

250 ml glacial acetic acid (CH_3COOH)

2000 ml distilled water

maximum weight of CdS precipitate in 75 ml (the capacity of the conventional gas scrubbers) of solution approximately 1.0 gram.

2) **Barium hydroxide solution** -

(absorbs carbon dioxide and traps it as insoluble $BaCO_3$)

80 gm Barium hydroxide ($Ba(OH)_2.8H_2O$)

1600 ml distilled water

Filter through No. 2 Whatman Filter Paper and store solution in sealed container.

maximum weight of $BaCO_3$ precipitate in 75 ml of solution approximately 2.2 grams.

APPENDIX E: SAMPLE CALCULATIONS OF GAS PRODUCTION DATA.

The amount of hydrogen sulfide or carbon dioxide released during each individual monitoring period was calculated from the weight of precipitate collected in the appropriate gas scrubber.

(1) Hydrogen Sulfide (H_2S)

Given: weight of dry cadmium sulfide (CdS) precipitate = x mg

time interval over which sulfide was collected = ΔT hr

molecular weight of H_2S = 34.08

molecular weight of CdS = 144.46

Then, the weight of sulfide (as hydrogen sulfide) collected =

$$\frac{34.08}{144.46} \times \text{mg} = 0.236 \times \text{mg } H_2S$$

and the rate of production of hydrogen sulfide over the collection period = $\frac{0.236x}{\Delta T} \ \frac{\text{mg}H_2S}{\text{hr}}$

(2) Carbon Dioxide (CO_2)

Given: weight of dry barium carbonate ($BaCO_3$) precipitate = x mg

time interval over which carbon dioxide was collected = ΔT hr

molecular weight of CO_2 = 44.00

molecular weight of $BaCO_3$ = 197.35

Then, the weight of carbon dioxide collected =

$$\frac{44.00}{197.35} \times \text{mg} = 0.223 \times \text{mg } CO_2$$

and the rate of production of carbon dioxide over the collection period = $\frac{0.223\,x}{\Delta T} \ \frac{\text{mg } CO_2}{\text{hr}}$.

APPENDIX F: SUMMARY OF CALCULATIONS AND LOGIC INVOLVED IN ESTIMATING THE RATES OF APPLICATION OF CHEMICALS TO BE USED IN THE INCUBATION TRIALS.

The methods employed to estimate the amounts of chemicals required for effective sulfide control are summarized on the following pages. All calculations are based on a weight of manure to be treated equal to 2000 grams.

(1) Trial I:

(a) Ferrous plus metallic iron

Add sufficient Fe^{++} as $FeCl_2.4H_2O$ to react with 100 ppm S expected to be in the manure at the time of chemical additions.

Add sufficient Fe^{0} as a finely ground powder to react with 1500 ppm S, assuming that four times as much iron is corroded as is bound as iron sulfide.

In both cases, assume that sulfide is precipitated by iron as FeS.

Given the following atomic and formula weights:

$FeCl_2.4H_2O$	198.83
Fe	55.85
S	32.06

Then, amount of $FeCl_2.4H_2O$ required is

$$(100 \times 10^{-6})(2000)\left(\frac{198.83}{32.06}\right) = 1.24 \text{ grams}$$

Amount of Fe^{0} required is

$$(1500 \times 10^{-6})(2000)\left(\frac{55.85}{32.06}\right)(4) = 20.90 \text{ gms}$$
$$\approx 20 \text{ grams.}$$

(b) Ferric iron

Add sufficient Fe^{+++} as $FePO_4$ to react with 1500 ppm S. Assume that Fe^{+++} is first reduced to Fe^{++} and then reacts with S to yield FeS.

Given the following formula and atomic weights:

$FePO_4$	150.82
S	32.06

Then, amount of $FePO_4$ required is

$$(1500 \times 10^{-6})(2000)(\frac{150.82}{32.06}) = 14.11 \text{ grams.}$$

Allowing an excess equal to the calculated amount, weight of $FePO_4$ = 28.22 grams.

(c) Metallic iron

Add 20 grams of Fe^{0} as a finely ground powder as calculated in (a) above.

(d) Lime

Hammond et al. (56) reported that o.15 lb. of hydrated lime is required to raise the pH of the daily excretion of one pig to greater than 10. Assume an average daily production of excreta from one pig equal to 10 lb.

Then, the amount of lime required is

$$(\frac{0.15}{10})(2000) = 30 \text{ grams.}$$

(e) **Nitrate**

Add nitrate, as $NaNO_3$, to achieve the molar concentration of nitrate equal to the molar concentration of sulfate which would be reduced to yield 1500 ppm S in the manure.

Given the following formula and atomic weights:

$NaNO_3$	85.00
S	32.06.

Then, the amount of $NaNO_3$ required is

$$\left(\frac{85.00}{32.06}\right)(1500 \times 10^{-6})(2000) = 7.95 \text{ grams.}$$

Allowing a small excess of 1/3 the calculated amount, weight of $NaNO_3$ = 10.60 grams.

(2) Trial II:

(a) **Ferrous plus metallic iron**

As for the same treatment in Trial I except:

(i) add only half as much $FeCl_2.4H_2O$ or 0.62 gm.

(ii) add metallic iron as an iron rod instead of as a powder.

(b) **Metallic iron**

As for the same treatment in Trial I.

(c) **Lime**

As for the same treatment in Trial I except add only 2/3 as much $Ca(OH)_2$, or 20 gm.

(3) Trial III:

(a) Ferric iron

Add sufficient Fe^{+++} as $Fe_2(SO_4)_3.nH_2O$ to react with 350 ppm S. As in Trial I, assume Fe^{+++} is first reduced to Fe^{++} and then reacts with S to yield FeS.

Given the following formula and atomic weights:

$Fe_2(SO_4)_3.nH_2O$(79% $Fe_2(SO_4)_3$)	506.18
S	32.06
Fe	55.85

Then, the amount of chemical required is

$$(\frac{506.18}{32.06})(\frac{1}{2})(350 \times 10^{-6})(2000) = 5.52 \text{ gm.}$$

(b) Metallic iron

As for the same treatment in Trial I except add Fe^0 as an iron rod instead of as a finely ground powder.

(c) Persulfate

Initial work in Sweden (74) has indicated that ammonium persulfate effectively controls odors from manure if added at the rate of 17 Kg/ton of manure.

Then, the amount of $(NH_4)_2S_2O_8$ required is

$$(\frac{17}{1000}\frac{Kg}{Kg})(2000 \text{ gm}) = 34 \text{ gm.}$$

However, a recent report (110) has suggested that much lower rates of application are effective.

Therefore, add 20 gm of $(NH_4)_2S_2O_8$.

(d) Permanganate

Faith (45) recommended that $KMnO_4$ be applied to manure as an aqueous solution. Since the total volume of chemical addition had been set at 100 ml for these trials, 100 ml of $KMnO_4$ was added. Amount of $KMnO_4$ required = 2 gm.

(e) Nitrate

Add nitrate, as $NaNO_3$, on an equal oxygen basis with the ammonium persulfate in (c) above.

Given, the following formula and atomic weights:

$(NH_4)_2S_2O_8$	228.20
$NaNO_3$	85.00
O	16.00

Then, the amount of $NaNO_3$ required is

$$\left(\frac{85}{48}\right)\left(\frac{128}{228.2}\right)(20) = 19.87 \text{ gm.}$$

(4) Trial IV:

(a) Metallic iron

As for the same treatment in Trial III.

(b) Persulfate

As for the same treatment in Trial III.

(c) Permanganate

Add 5 gm solid $KMnO_4$.

APPENDIX G: NITROGEN INTAKE AND EXCRETION BY FEEDER PIGS.

The intake of feed and the output of feces and urine by feeder pigs receiving eight different diets during four three-day collection periods are given in the following Table. Data are also given on the nitrogen composition of the feed and the excreta. All of these data were provided by the Department of Animal Science, University of Alberta.

The eight different dietary treatments are numbered according to the diet received by the pigs as outlined in Appendix C. Treatments 2 to 7, inclusive, involved rapeseed whereas treatments 1 and 8 did not. The collection periods are numbered consecutively from 1 to 4.

Treatment	Collection Period	Dry Feed gm	Dry Feed %N	Dry Feces gm	Dry Feces %N	Urine ml	Urine %N
1	1	4461	2.67	784.5	2.85	11420	0.44
1	2	3272	2.66	456.5	2.06	3390	0.87
1	3	4250	2.61	685.8	2.36	7860	0.72
1	4	4434	2.61	654.1	2.52	3780	1.04
2	1	3780	2.88	709.7	2.75	600	1.15
2	2	3275	2.86	526.6	2.42	14680	0.31
2	3	4195	2.83	786.4	2.55	8590	0.68
2	4	3158	2.81	552.4	2.42	1870	1.93
3	1	4329	2.72	833.5	2.86	5800	1.00
3	2	3662	2.70	570.3	2.65	3540	0.88
3	3	3970	2.69	749.8	2.49	8980	0.55
3	4	4295	2.68	717.0	2.25	4260	0.98
4	1	4245	2.89	841.2	3.17	12820	0.40
4	2	3118	2.86	505.0	2.36	31820	0.13
4	3	3910	2.86	765.2	2.47	4100	1.22
4	4	4193	2.84	701.0	2.51	6040	0.83
5	1	3776	2.82	674.9	2.72	22160	0.23
5	2	3673	2.81	607.2	2.77	3850	0.92
5	3	4575	2.78	926.1	2.81	2220	1.22
5	4	3640	2.78	682.5	2.78	2490	1.41
6	1	3153	2.80	587.5	2.62	2290	1.63
6	2	3646	2.80	616.8	2.52	7240	0.68
6	3	4135	2.77	869.0	2.70	6520	0.71
6	4	4060	2.76	626.0	2.34	28720	0.13
7	1	3542	2.80	768.8	2.96	5530	0.58
7	2	3222	2.80	543.5	2.52	4820	0.77
7	3	3810	2.77	668.7	2.82	12570	0.40
7	4	4388	2.76	731.4	2.63	12320	0.38
8	1	4777	2.76	799.2	2.99	8130	0.60
8	2	4001	2.75	693.8	3.17	11070	0.37
8	3	4230	2.73	794.4	2.46	4060	1.04
8	4	3456	2.73	480.8	2.47	5350	0.69

APPENDIX H: SULFUR AND NITROGEN INTAKE AND EXCRETION BY FEEDER PIGS RECEIVING TWO DIFFERENT DIETS.

The intake of feed and the output of feces and urine by feeder pigs subjected to two different dietary treatments during four three-day collection periods are given in the following table. Values are also given for the nitrogen and sulfur composition of the feed and excreta. All data are on a per pig basis for a three-day feeding period.

Data on feed intake, output of excreta, and nitrogen composition of feed and excreta were calculated from values given in Appendix G for pigs subjected to eight different dietary treatments. The eight treatments were regrouped into those involving rapeseed and those not involving rapeseed, and mean values for these two treatments were calculated accordingly. Data on the sulfur composition of feed and excreta were obtained directly by analyzing composite samples of feed and excreta from the appropriate group of animals.

APPENDIX H: DATA ON NITROGEN AND SULFUR INTAKE AND EXCRETION BY FEEDER PIGS RECEIVING TWO DIFFERENT DIETS.

Treatment	Diets containing rapeseed				Diets not containing rapeseed			
Collection Period	1	2	3	4	1	2	3	4
Dry Feed:								
Feed intake (gm)	3804	3349	4099	3956	4619	3636	4240	3945
Total nitrogen (% d.b.)	2.82	2.81	2.78	2.77	2.72	2.71	2.67	2.66
Total sulfur (% d.b.)	0.29	0.29	0.29	0.29	0.23	0.23	0.23	0.23
Dry Feces:								
Fecal output (gm)	735.9	561.9	794.2	668.4	791.8	575.2	740.1	567.4
Total nitrogen (% d.b.)	2.87	2.55	2.64	2.49	2.92	2.73	2.41	2.50
Total sulfur (% d.b.)	0.345	0.302	0.262	0.330	0.315	0.319	0.307	0.334
Total sulfate-sulfur (ppm d.b.)	375	345	300	488	294	476	448	668
Urine:								
Urinary output (ml)	8200	10975	7163	9283	9775	7230	5960	4565
Total nitrogen (% d.b.)	0.48	0.36	0.65	0.44	0.53	0.49	0.83	0.83
Total sulfur (ppm d.b.)	476	686	520	1128	420	536	740	662
Total sulfate-sulfur (ppm d.b.)	492	668	530	1040	410	594	820	748

APPENDIX I: PHYSICAL AND CHEMICAL CHARACTERISTICS OF SWINE MANURE AND WASTEWATER SAMPLES.

The data obtained from analyses of manure and wastewater samples for total solids, pH, color, total nitrogen, total sulfur, and water-soluble sulfate-sulfur are shown on the following pages. The following abbreviations are used to identify the laboratory in which the analyses were performed:

AEL	Agricultural Engineering Laboratory, Department of Agricultural Engineering, University of Alberta.
SFTL	Alberta Soil and Feed Testing Laboratory, O.S. Longman Building, Edmonton.
SSL	Soil Science Laboratory, Department of Soil Science, University of Alberta.

(a) Total Solids Content (%)

Sample	AEL 1	AEL 2	SFTL 1	SFTL 2	Mean of four values
A-0501	4.74	4.94	4.41	4.35	4.61
A-0528	9.52	9.59	9.54	9.40	9.51
A-0707	6.31	6.41	7.18	6.84	6.68
A-0707-a	6.35	6.60	6.49	6.45	6.47
A-0707-n	-*	-*	6.78	6.61	6.70
A-0811	6.08	5.93	1.82**	5.95	5.99
A-0811-n	5.2	5.0	4.81	5.09	5.02
A-1108	8.07	8.12	8.54	8.45	8.30
B-0522-L	0.31	0.33	0.13	0.13	0.22
B-0522-S	7.42	7.54	7.53	7.60	7.52
B-0522	0.85	0.99	0.83	0.74	0.85
B-0529	1.18	1.24	1.04	0.92	1.10
C-0523	5.97	6.11	5.81	5.59	5.87
C-0907	2.86	3.04	3.14	3.14	3.04
C-0907-a	2.75	2.81	2.70	2.75	2.75
C-0907-n	2.79	2.75	2.75	2.86	2.79
C-1015	3.67	3.59	4.05	4.25	3.89
C-0907-nb	2.72	2.85	3.16	3.07	2.95

* No data obtained.

** Value not included in calculation of mean since it is much lower than other recorded values.

(b) pH.

Sample	AEL	S.F.T.L. 1	 2	 Mean
A-0501	-*	6.6	6.5	6.55
A-0528	6.4	5.4	5.4	5.4
A-0707	6.6	6.6	6.6	6.6
A-0707-a	8.1	7.4	7.4	7.4
A-0707-n	6.5	6.0	6.0	6.0
A-0811	6.7	6.6	6.6	6.6
A-0811-n	6.5	7.0	7.0	7.0
A-1108	6.65	6.5	6.5	6.5
B-0522-L	7.7	8.1	8.3	8.2
B-0522-S	7.6	7.7	7.5	7.6
B-0522	6.5	7.4	7.5	7.45
B-0529	6.6	7.4	7.2	7.3
C-0523	6.9	7.0	6.7	6.85
C-0907	6.6	7.1	7.2	7.15
C-0907-a	-*	8.4	8.4	8.4
C-0907-n	6.8	7.3	7.3	7.3
C-1015	6.5	6.8	6.8	6.8
C-0907-nb	6.4	6.7	6.6	6.65

* No data obtained.

(c) Color.

Sample	Color
A-0501	Black-green
A-0528	Black-green
A-0707	Black-green
A-0707-a	Brown-green
A-0707-n	Black-green
A-0811	Black-green
A-0811-n	Black-green
A-1108	Black-green
B-0522-L	Red-brown
B-0522-S	Black
B-0522	Green
B-0529	Green
C-0523	Green-brown
C-0907	Green-brown
C-0907-a	Brown-green
C-0907-n	Black-green
C-1015	Green-brown
C-0907-nb	Black-green

(d) Total Nitrogen (% w.b.)

Sample	1	2	Mean
A-0501	0.268	0.266	0.267
A-0528	0.342	0.335	0.338
A-0707	0.270	0.270	0.270
A-0707-a	0.208	0.212	0.210
A-0707-n	0.254	0.264	0.259
A-0811	0.257	0.264	0.260
A-0811-n	0.278	0.271	0.274
A-1108	0.371	0.358	0.364
B-0522-L	0.038	0.036	0.037
B-0522-S	0.256	0.257	0.256
B-0522	0.085	0.083	0.084
B-0529	0.098	0.100	0.099
C-0523	0.306	0.310	0.308
C-0907	0.241	0.238	0.240
C-0907-a	0.216	0.202	0.210
C-0907-n	0.245	0.244	0.244
C-1015	0.302	0.312	0.307
C-0907-nb	0.256	0.244	0.250

(e) Total Sulfur (ppm wb).

Sample	SSL	S.F.T.L.		Mean of three values
		1	2	
A-0501	303	262	282	282
A-0528	365	377	414	385
A-0707	304	270	280	285
A-0707-a	196	315	343	285
A-0707-n	218	254	212	228
A-0811	216	261	276	251
A-0811-n	210	245	252	236
A-1108	346	318	328	331
B-0522-L	82	38*	68	75
B-0522-S	872	328	128	443
B-0522	188	84	76	116
B-0529	235	88	112	145
C-0523	270	269	266	268
C-0907	163	158	174	165
C-0907-a	188	192	202	194
C-0907-n	175	175	179	176
C-1015	240	250	266	252
C-0907-nb	173	151	150	158

* Value not included in calculation of mean since it is lower than the values for SO_4-S of the same sample.

(f) Water-soluble sulfate-sulfur (ppm w.b.)

Sample	1	2	Mean
A-0501	122	124	123
A-0528	124	116	120
A-0707	64	60	62
A-0707-a	54	54	54
A-0707-n	58	50	54
A-0811	48	46	47
A-0811-n	46	54	50
A-1108	46	46	46
B-0522-L	68	64	66
B-0522-S	68	70	69
B-0522	54	54	54
B-0529	54	50	52
C-0523	150	162	156
C-0907	78	70	74
C-0907-a	66	68	67
C-0907-n	80	84	82
C-1015	128	144	136
C-0907-nb	144	144	144

APPENDIX J: GAS PRODUCTION DATA FOR LABORATORY INCUBATION TRIALS.

Gas production data obtained during the laboratory incubation trials involving chemical treatment of manure are shown on the following pages. Data for each of the four trials are given on separate pages. Gas production parameters for which data were collected are identified in the Tables as follows:

A. Total sulfides evolved during each collection period, given as mg H_2S. The figure given in the "elapsed time" column is the time, in days and hours, from the beginning of the incubation trial to the end of the respective collection period.

B. Rate of evolution of sulfides during each collection period, given as mg H_2S/hr. The figure given in the "elapsed time" column is the time,in days and hours, from the beginning of the incubation trial to the middle of the respective collection period.

C. Cumulative evolution of sulfides to the end of each collection period given as mg H_2S. The figure given in the "elapsed time" column is the time, in days and hours, from the beginning of the incubation trial to the end of the respective collection period.

D. Rate of evolution of carbon dioxide, given as mg CO_2/hr. The figure given in the "elapsed time" column is the time, in days and hours, from the beginning of the incubation trial to the middle of the carbon-dioxide monitoring period.

Trial I

Parameter monitored	Elapsed time (days-hours)	Treatment					
		Control	Lime	Fe^{++} + Fe^{0}	Fe^{0} (powder)	NO_3^-	Fe^{+++}
A (mgH_2S)	1-21	44.37	46.73	38.23	39.41	45.55	49.80
	4-2	26.43	28.55	24.31	23.13	27.37	34.92
	6-0	40.36	2.60	2.36	10.86	17.00	11.10
	8-23	13.45	4.01	1.89	3.06	8.26	5.66
	13-2	20.53	2.13	1.89	1.42	8.73	2.83
	19-7	38.00	2.59	2.83	3.07	35.87	8.97
	24-22	20.06	14.40	3.07	2.83	25.72	17.70
B (mgH_2S/hr)	0-22	0.986	1.038	0.850	0.876	1.012	1.107
	2-23	0.504	0.544	0.463	0.440	0.521	0.665
	5-0	0.877	0.056	0.051	0.236	0.369	0.241
	7-11	0.189	0.056	0.026	0.043	0.116	0.080
	11-0	0.207	0.022	0.019	0.014	0.088	0.029
	16-4	0.255	0.017	0.019	0.021	0.241	0.060
	22-2	0.149	0.107	0.023	0.021	0.190	0.131
C (mgH_2S)	1-21	44.37	46.73	38.23	39.41	45.55	49.80
	4-2	70.80	75.28	62.54	62.54	72.92	84.72
	6-0	111.16	77.88	64.90	73.40	89.92	95.82
	8-23	124.61	81.89	66.79	76.46	98.18	101.48
	13-2	145.14	84.02	68.68	77.88	106.91	104.31
	19-7	183.14	86.61	71.51	80.95	142.78	113.28
	24-22	203.20	101.01	74.58	83.78	168.50	130.98
D ($mgCO_2/hr$)	1-21	16.40	17.75	16.31	16.18	17.50	17.42
	3-21	20.56	19.95	17.65	17.46	20.23	21.03
	6-0	16.86	0.00	9.47	11.09	13.80	6.80
	7-21	12.67	0.00	10.93	9.72	13.42	6.69
	9-23	13.06	0.00	12.23	12.23	10.39	8.16
	12-21	13.69	0.00	13.96	13.38	12.49	11.86
	15-21	14.27	0.00	17.22	15.21	12.58	11.55
	19-7	24.35	0.00	30.48	26.29	19.41	22.09
	21-21	16.39	0.00	15.11	15.22	12.88	13.77
	22-21	16.06	0.00	11.92	14.67	10.66	11.15

Trial II

Parameter monitored	Elapsed time (days-hours)		Treatment		
		Fe^0 (powder)	Control	$Fe^{++}+Fe^0$	Lime
A (mgH_2S)	1-18	31.39	29.26	29.03	20.77
	3-20	29.50	28.09	29.26	15.57
	5-21	12.27	15.81	2.83	14.40
	9-23	12.98	26.20	4.72	16.05
	12-22	9.21	20.06	4.96	9.91
	15-22	4.72	13.68	3.30	5.66
	21-14	5.19	13.69	4.25	9.68
B (mgH_2S/hr)	0-21	0.756	0.705	0.700	0.500
	2-19	0.578	0.551	0.574	0.305
	4-21	0.254	0.328	0.059	0.298
	7-22	0.132	0.267	0.048	0.163
	11-11	0.129	0.281	0.069	0.139
	14-10	0.066	0.191	0.046	0.079
	18-18	0.038	0.101	0.031	0.071
C (mgH_2S)	1-18	31.39	29.26	29.03	20.77
	3-20	60.89	57.35	58.29	36.34
	5-21	73.16	73.16	61.12	50.74
	9-23	86.14	99.36	65.84	66.79
	12-22	95.35	119.42	70.80	76.70
	15-22	100.07	133.10	74.10	82.36
	21-14	105.26	146.79	78.35	92.04
D ($mgCO_2/hr$)	1-17	18.45	16.11	14.94	14.72
	3-16	15.02	14.17	7.38	13.73
	5-16	8.47	-	10.06	2.28
	6-15	-	8.08	8.72	2.48
	9-19	7.66	8.50	-	2.05
	12-23	7.02	7.47	6.73	1.75
	15-22	5.98	5.52	5.48	1.57
	18-0	5.84	5.00	5.40	1.25
	20-14	4.46	3.05	3.53	0.78

Trial III

Parameter monitored	Elapsed time (days-hours)	Treatment					
		$S_2O_8^=$	NO_3^-	MnO_4^-	Fe^o(rod)	Fe^{+++}	Control
A (mgH_2S)	1-17	19.59	19.59	17.94	18.64	17.94	20.53
	3-22	20.53	21.95	20.06	20.30	19.11	18.88
	5-20	0.00	12.74	0.00	19.59	4.25	19.35
	7-22	0.00	0.00	3.54	14.16	4.72	13.93
	10-18	0.00	2.36	4.95	12.98	3.54	14.16
	13-18	0.00	6.14	7.32	11.09	3.54	12.74
	16-22	0.00	5.66	9.67	11.09	4.72	11.80
	20-17	0.00	6.14	13.93	12.04	4.48	12.75
B (mgH_2S/hr)	0-21	0.478	0.478	0.438	0.455	0.438	0.501
	2-19	0.391	0.418	0.382	0.387	0.364	0.360
	4-21	0.000	0.271	0.000	0.417	0.090	0.412
	6-22	0.000	0.000	0.071	0.283	0.094	0.278
	9-8	0.000	0.034	0.073	0.191	0.052	0.208
	12-6	0.000	0.086	0.102	0.155	0.050	0.178
	15-8	0.000	0.075	0.128	0.147	0.062	0.156
	18-19	0.000	0.067	0.153	0.132	0.049	0.140
C (mgH_2S)	1-17	19.59	19.59	17.94	18.64	17.94	20.53
	3-22	40.12	41.54	38.00	38.94	37.05	39.41
	5-20	40.12	54.28	38.00	58.53	41.30	58.76
	7-22	40.12	54.28	41.54	72.69	46.02	72.69
	10-18	40.12	56.64	46.49	85.67	49.56	86.85
	13-18	40.12	62.78	53.81	96.76	53.10	99.59
	16-22	40.12	68.44	63.48	107.85	57.82	111.39
	20-17	40.12	74.58	77.41	119.89	62.30	124.14
D ($mgCO_2$/hr)	1-13	15.06	19.78	15.53	13.22	14.69	12.80
	3-16	11.77	13.47	13.02	12.09	10.84	11.42
	5-16	8.28	9.78	8.45	9.31	7.72	8.58
	7-18	6.13	10.30	6.80	6.13	6.13	7.25
	10-13	5.02	13.66	5.61	5.05	4.57	5.43
	13-13	3.16	8.96	5.69	-	4.16	4.83
	16-16	3.14	6.74	5.19	4.33	3.57	4.16
	19-22	3.14	7.41	5.78	4.15	3.63	4.37

Trial IV:

Parameter monitored	Elapsed time (days-hours)	Treatments			
		Fe^{0}(rod)	Control	$S_2O_8^{=}$	MnO_4^{-}
A (mgH$_2$S)	2-2	41.30	39.65	44.13	38.23
	4-9	27.85	29.26	24.78	24.78
	6-8	29.03	30.68	3.54	7.79
	8-10	20.29	21.95	0.39	8.02
	11-4	15.11	16.52	0.52	8.50
	15-8	13.92	17.46	0.74	2.12
	19-4	8.73	12.51	0.74	1.42
B (mgH$_2$S/hr)	1-1	0.818	0.785	0.874	0.757
	3-4	0.511	0.537	0.455	0.455
	5-8	0.624	0.660	0.076	0.167
	7-9	0.406	0.439	0.008	0.160
	9-19	0.229	0.250	0.008	0.129
	13-6	0.139	0.175	0.008	0.021
	17-6	0.094	0.135	0.008	0.015
C (mgH$_2$S)	2-2	41.30	39.65	44.13	38.23
	4-9	69.15	68.91	68.91	63.01
	6-8	98.18	99.59	72.45	70.80
	8-10	118.47	121.54	72.84	78.82
	11-4	133.58	138.06	73.36	87.32
	15-8	147.50	155.52	74.10	89.44
	19-4	156.23	168.03	74.84	90.86
D (mgCO$_2$/hr)	2-0	31.11	32.34	33.45	32.78
	4-5	17.39	20.20	20.52	18.35
	6-4	16.72	14.94	11.82	19.18
	8-3	16.06	14.34	5.86	14.59
	11-0	12.24	12.52	5.43	12.41
	15-2	10.26	9.37	3.39	13.34
	18-19	10.53	9.19	3.08	15.11